

# Airborne Particulate Monitoring

**Greg Smallwood**



**Renewable Energy and Climate Science for the Americas:  
Metrology and Technology Challenges**

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# Acknowledgements

Jeff Brook

Environment Canada

Allan Bertram

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Greg Evans

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Jason Olfert

University of Alberta

Adam Boies

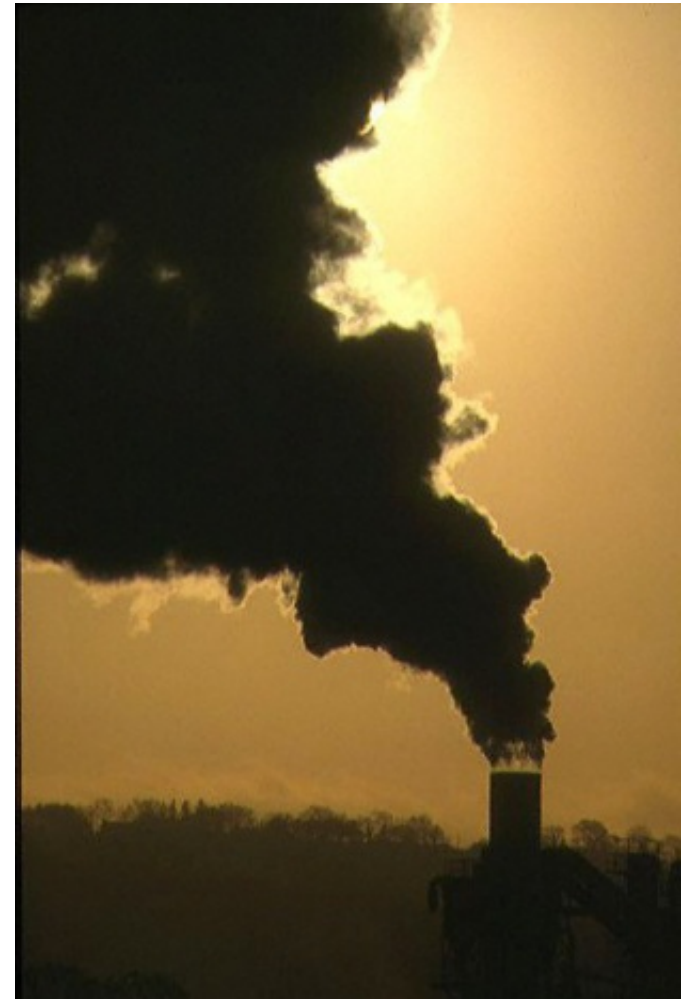
University of Cambridge

Kevin Thomson and the entire Black Carbon Metrology Team at NRC Measurement Science and Standards

# Overview

## Questions to be addressed:

- What are airborne particulates?
- What is the relevance of airborne particulates?
- What needs to be measured?
- What is the Canadian perspective on research and monitoring of airborne particulates?
- What is Canada doing about the measurement of black carbon?

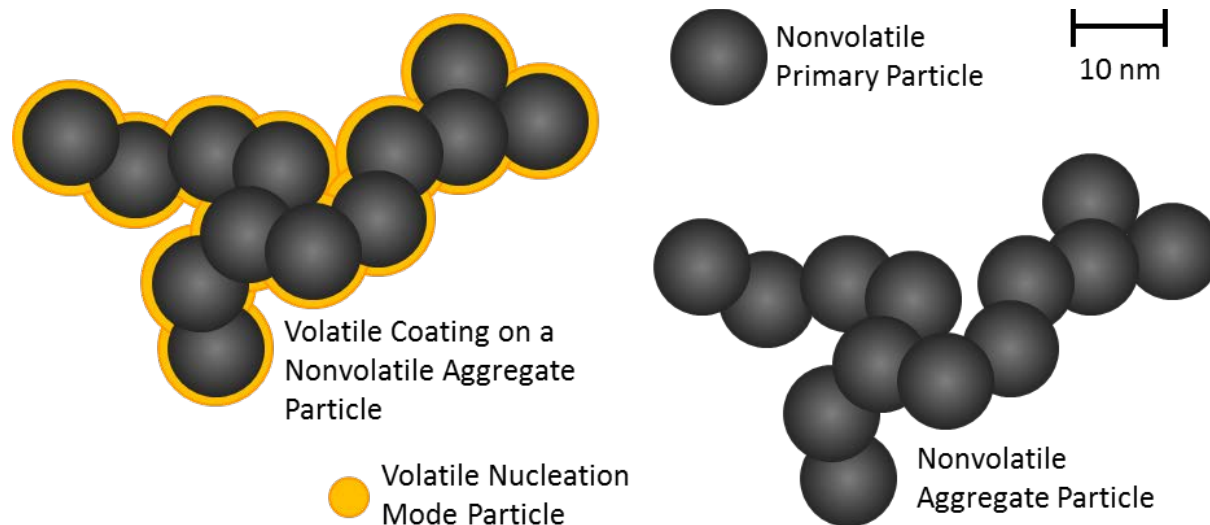


Allan Bertram, University of British Columbia

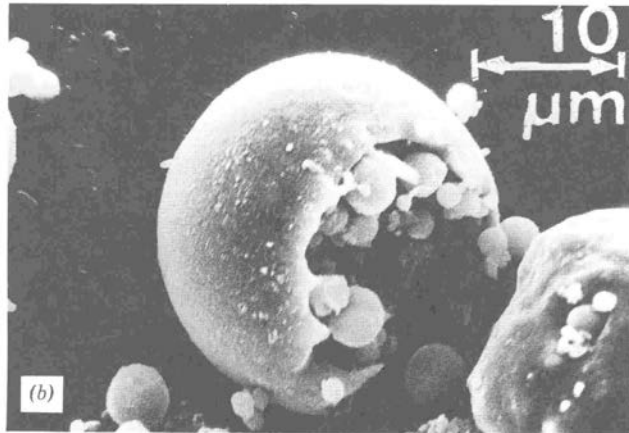
# What are Airborne Particulates?

## Description

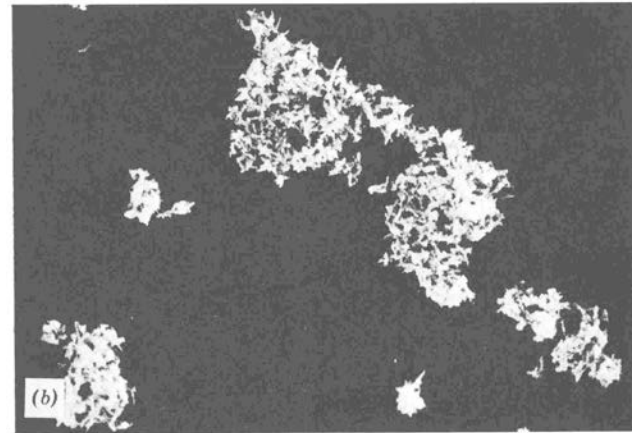
- airborne particulates are referred to as aerosols, nanoaerosols, particulate matter (PM)
- exist as a condensed phase in a gaseous medium
- can be liquid or solid, and volatile, semi-volatile, or nonvolatile



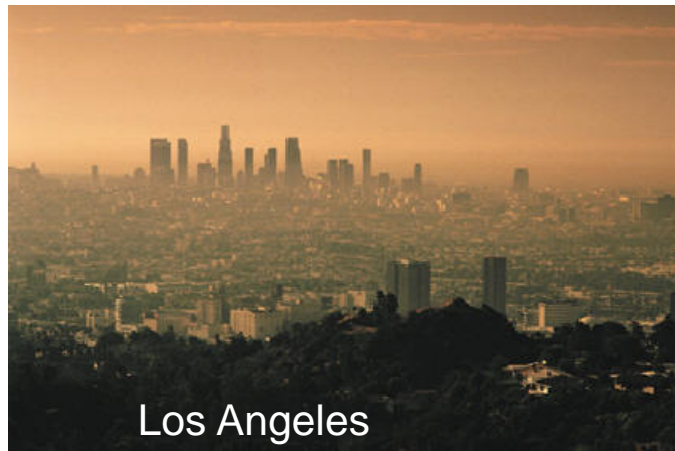
# Examples of Particulate Matter (PM)



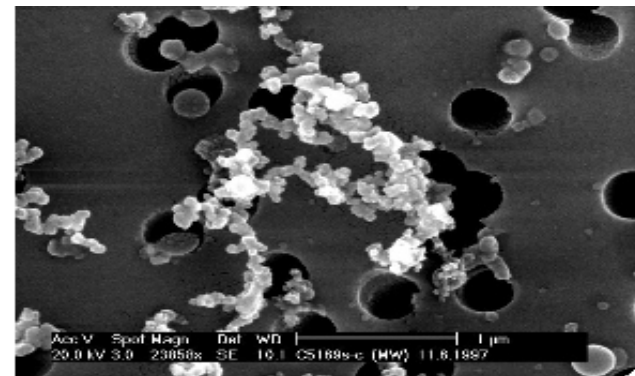
Coal fly ash (~10  $\mu\text{m}$ )



Iron-oxide particles from arc welding (~10  $\mu\text{m}$ )



Los Angeles  
Smog (~1-1000 nm)

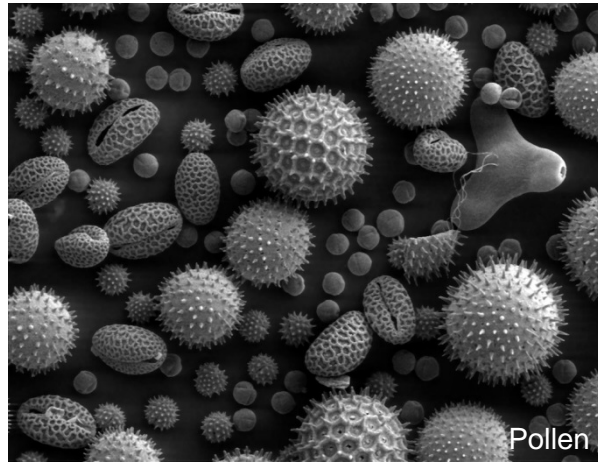


Diesel soot particles (~100 nm)

Jason Olfert, University of Alberta

# Natural/Biogenic Sources

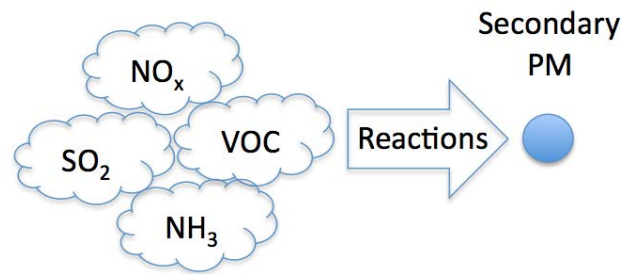
Forest fires, volcanoes, soil dust, sea salt, botanical debris...



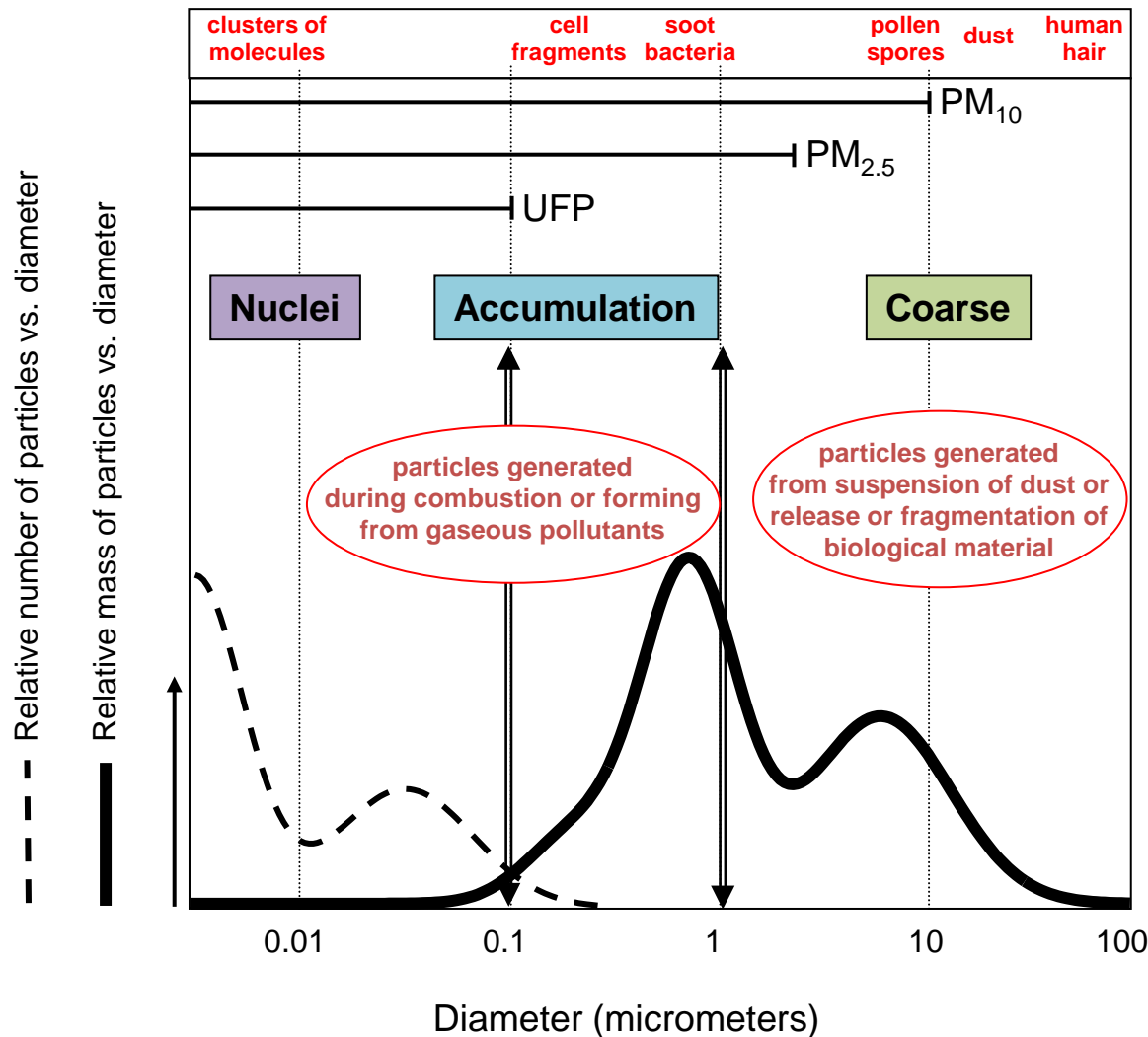
Jason Olfert, University of Alberta

# Anthropogenic Sources

Power plants, automobiles (engine exhaust, tires, brakes etc), fireplaces, deep-fryers, aircraft, inhalers...



# Airborne Particles Come in a Variety of Sizes



## Sizes

- 1 nm – 100 μm in diameter

## Concentrations

- $10^6$ - $10^9$  particles/cm<sup>3</sup> in urban environments
- $10^2$  particles/cm<sup>3</sup> remote regions



# Atmospheric Particle Composition

## Elemental carbon particles:

- produced during combustion

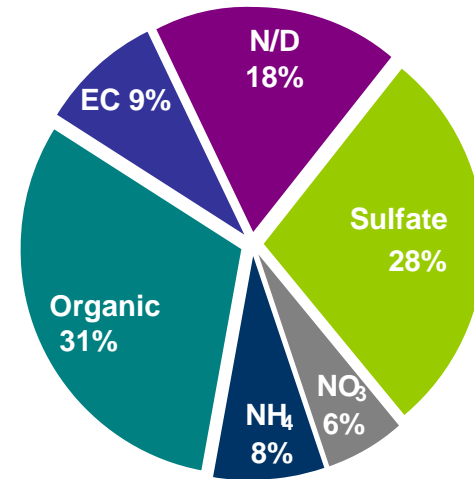
## Organic particles:

- primary organic particles
  - emitted directly to the atmosphere
- secondary organic particles
  - formed in the atmosphere by oxidation and condensation of volatile organic carbon
  - often requires photochemistry

## Sulfates

- ammonium sulfate particles
- mixed ammonium sulfate-organic particles

## Nitrates



## Typical Chemical Composition of Fine Aerosol (<1 $\mu$ m) in an Urban Area [Heintzenberg, 1989]

EC = Elemental carbon particles

N/D = not determined

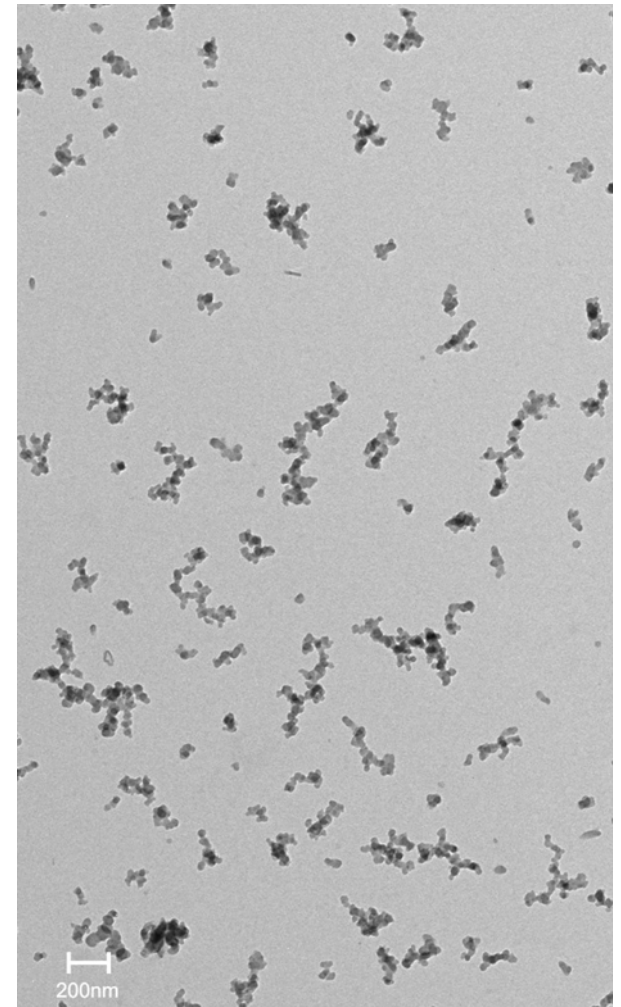
# What is the relevance of airborne particulates?

## Air Quality

- Human Health
- Visibility

## Climate Impacts

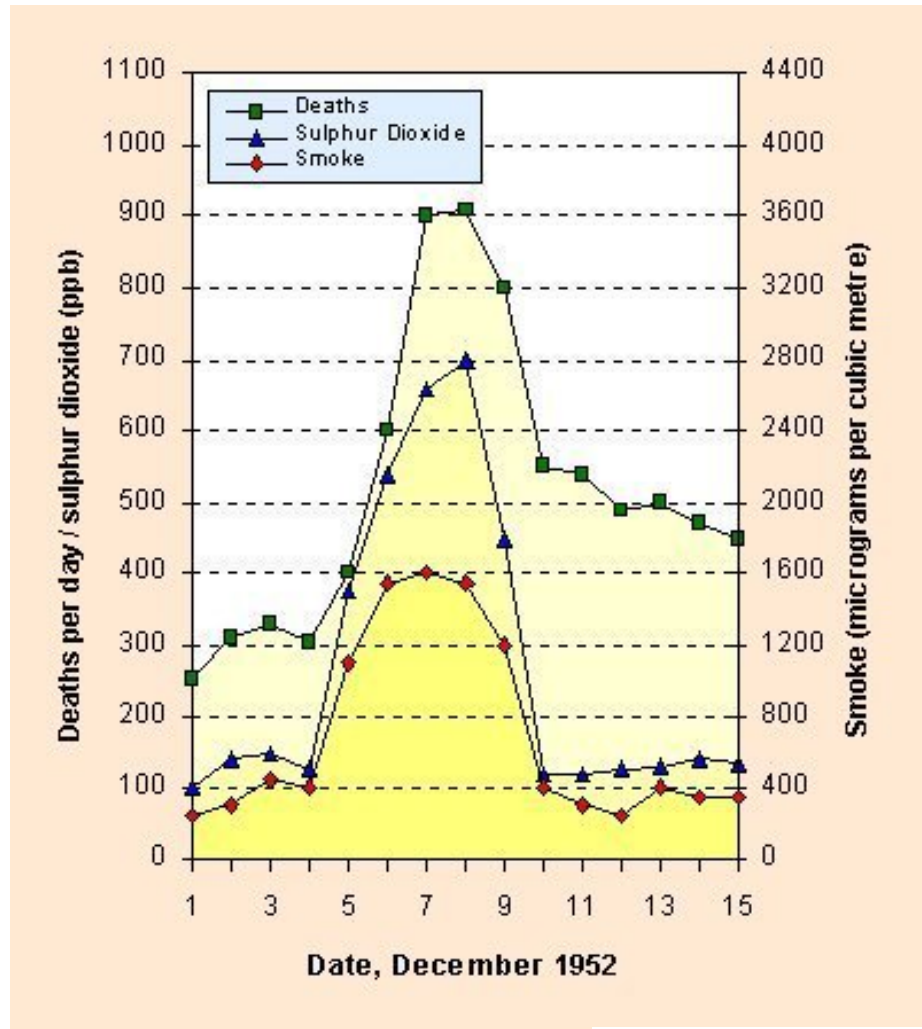
## Quality of Life and Economic Impacts



# Trigger for Health Effects of Airborne Particulates



London Smog Episode:  
5-9 Dec 1952



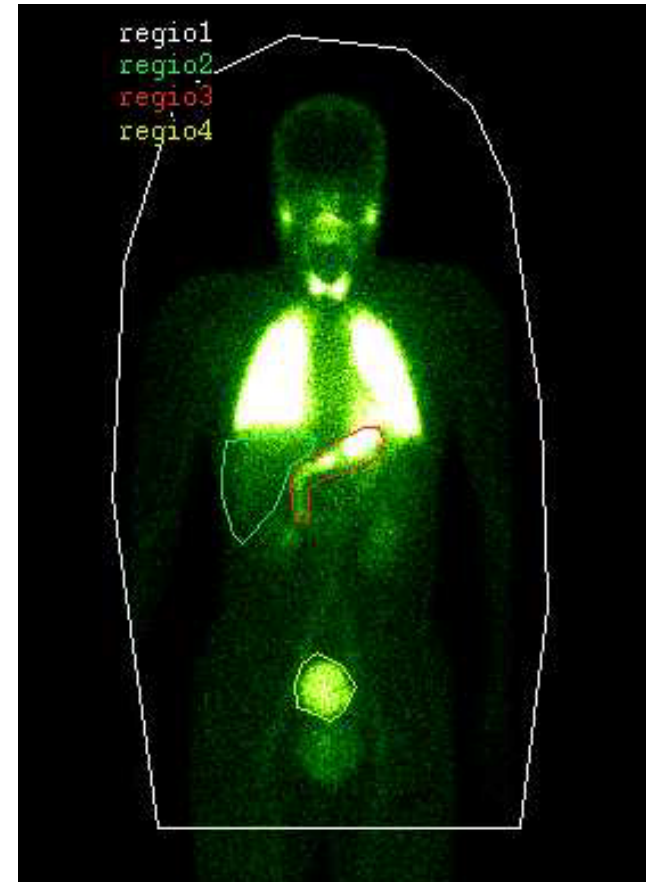
Greg Evans, University of Toronto

# Air Quality and Toxicology

## Toxicity is dependent on particle size

- different sizes of particles deposit in different area of the respiratory tract
- epidemiological studies have shown that acute exposure to high levels of ambient PM increase mortality rates about 1% for every  $5 \mu\text{g}/\text{m}^3$  increase in  $\text{PM}_{2.5}$
- about 70% of these deaths are due to cardiovascular disease, and 30% due to respiratory
- also increases in hospitalizations due to asthma and other respiratory diseases

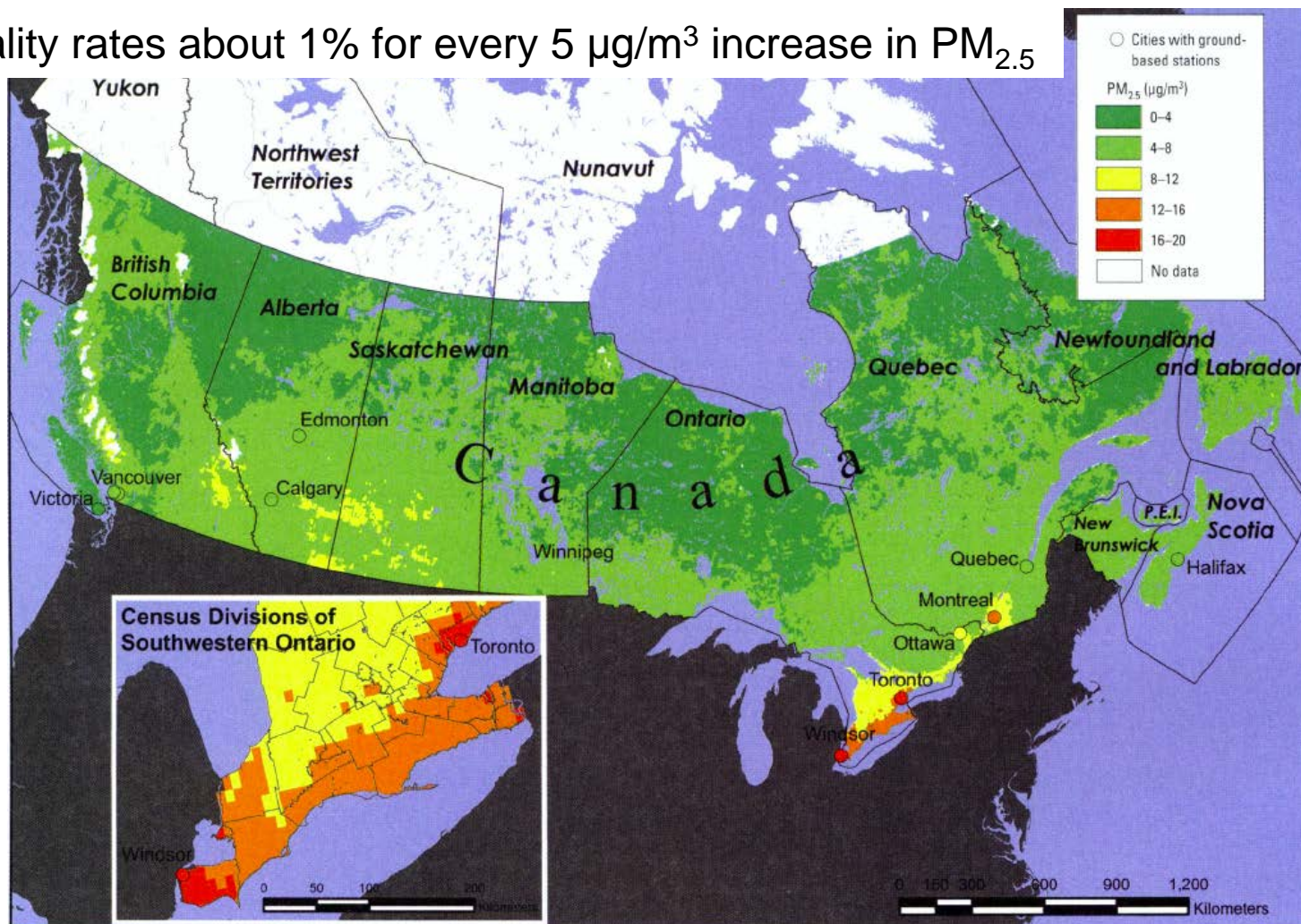
Gamma camera image shows particles accumulate in the nasal passages, lungs, liver, and bladder in minutes



Nemmar et al., *Circulation*, 2002

# PM<sub>2.5</sub> exposure and cardiovascular mortality: Canada

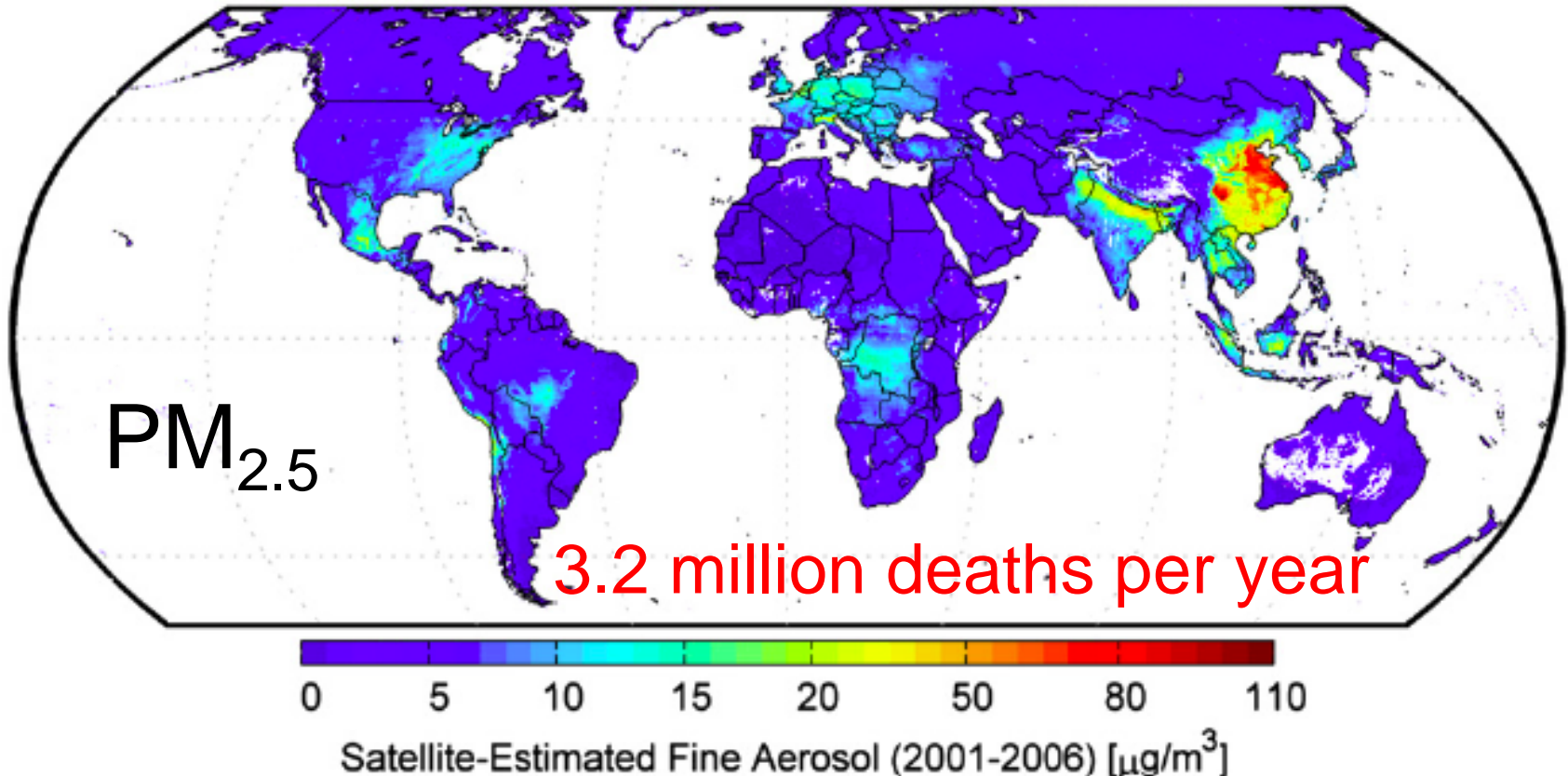
mortality rates about 1% for every 5  $\mu\text{g}/\text{m}^3$  increase in PM<sub>2.5</sub>



Crouse et al EHP May 2012

Greg Evans, University of Toronto

# PM<sub>2.5</sub> exposure and cardiovascular mortality: Global



Adult Mortality 8% (5.5-10.5)

Cardiopulmonary disease 12.8% (5.9-18.5)

*Evans J et al Env Res 2013*

Greg Evans, University of Toronto

# Air Quality and Visibility

Aerosols in the atmosphere absorb and scatter light which reduces visibility



Jeff Brook, Environment Canada

# How do aerosols affect climate?

Aerosols directly affect the global climate by absorbing and scattering solar radiation.

Aerosols indirectly affect the global climate by changing the properties of clouds - increases their albedo and lifetime.



- example of indirect effect is ship tracks

<http://www.wjla.com/pictures/2011/07/daily-eye-wonder---july-2011/ship-contrails-in-pacific-5508-366.html>

Allan Bertram, University of British Columbia



# Global aircraft black carbon (BC) emissions



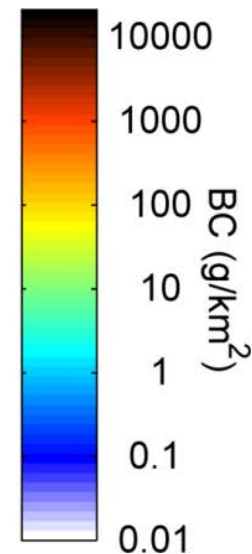
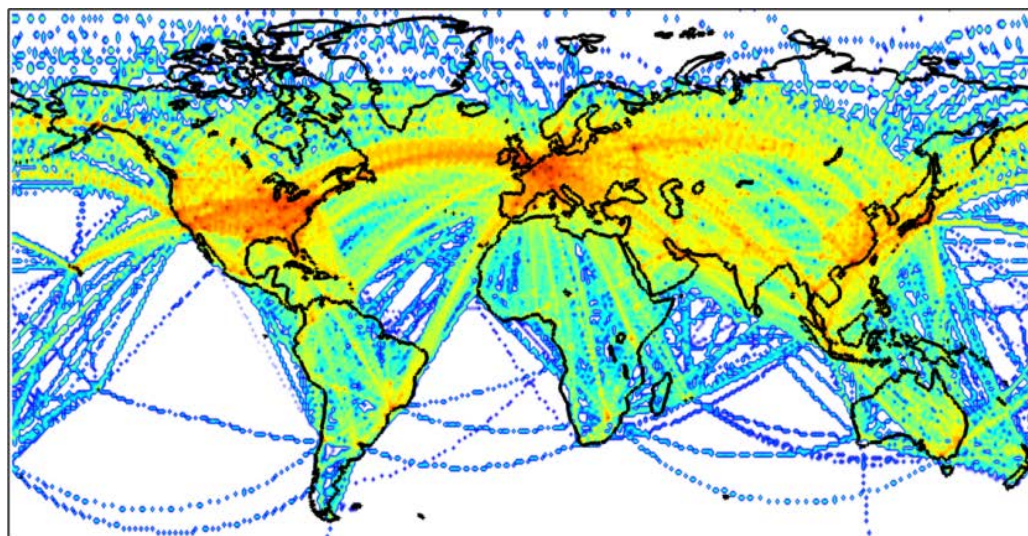
1960's



1980's



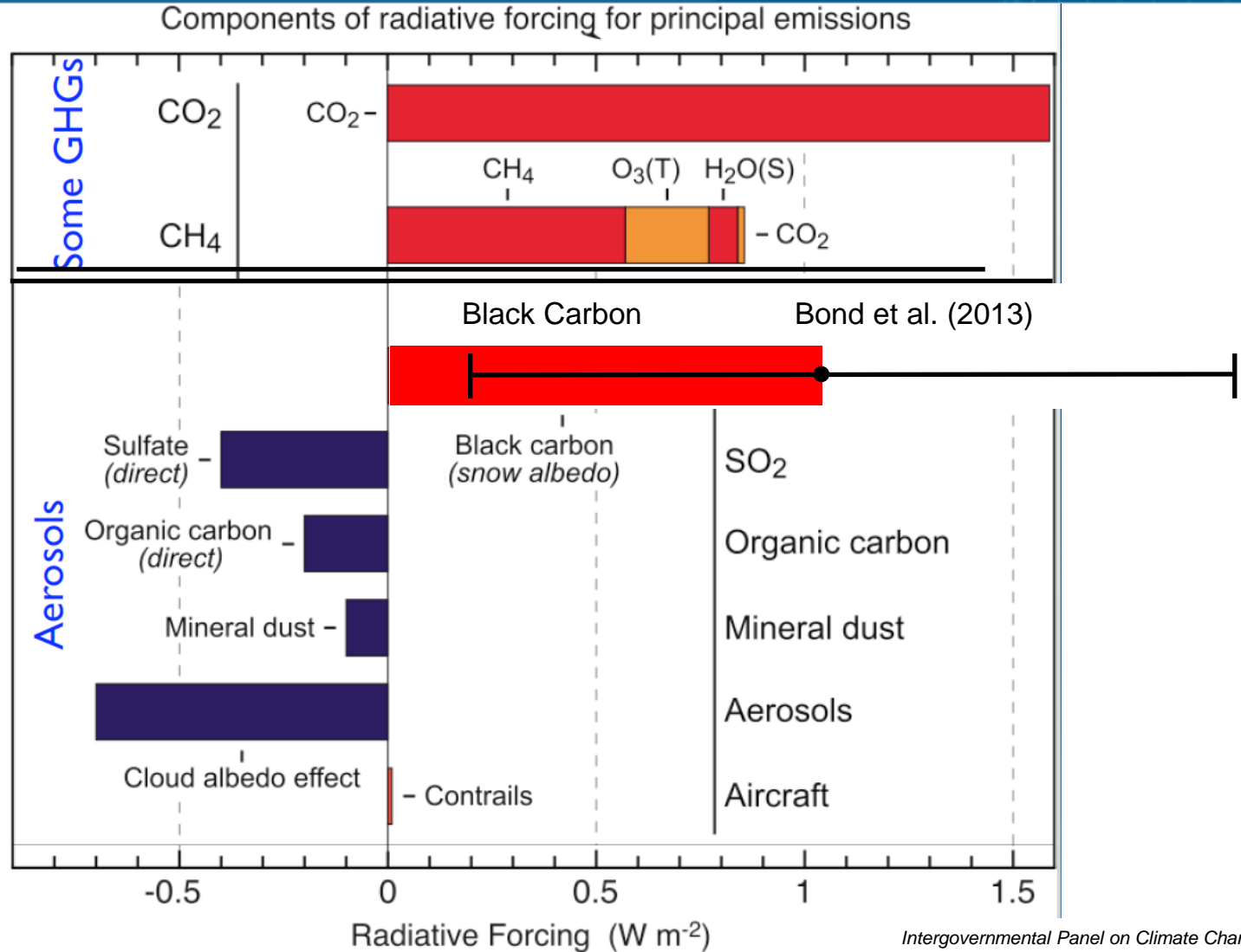
2000's



Stettler et al., (2013). *Environ. Sci. Technol.* doi.org/10.1021/es401356v

Adam Boies, University of Cambridge

# Relative Effect of Aerosols on Climate



# Impacts of Black Carbon

- BC is the most **light-absorbing** nano-aerosol
- BC absorbs 680x more energy by mass than CO<sub>2</sub>
- BC is a key contributor to **global warming**
- BC effects are **stronger in sensitive regions**, i.e. faster ice and snow melt in the Canadian Arctic
- BC mitigation could **rapidly slow** the rate of climate change, by up to 40% within 20 years

## For BC and related combustion emissions, on a global scale

- “the adoption of aggressive standards by 2015 would annually prevent the deaths of 200,000 people, save 13 million tons of grain and \$1.5 trillion in health damages after 2030.”

*Shindell et al, 2011, Nature Climate Change, 1, 59-66*

# What needs to be measured?

- regulated gaseous pollutants are specific
  - CO<sub>2</sub>, CO, SO<sub>2</sub>, NO<sub>x</sub>, HC, etc.
  - measurement of gaseous concentration
- current regulatory focus for PM is mass concentration in most jurisdictions
- Europe has added number concentration for on-road vehicle emissions
- health and environmental researchers and policymakers are asking for more specificity on PM
  - size and size distribution
  - composition
  - surface area and surface reactivity
  - optical properties (absorption and scattering)

# Measurement Issues (I)

## Traceability

- many instruments offer no opportunity for traceability
- filter-based mass can be traceable
  - issues with sensitivity (mass of particulate vs. mass of filter)
  - issues with filter artifacts
    - gaseous adsorption
    - fibre loss
    - less than 100% removal efficiency
  - issues with size cutoff
    - impactors and cyclones do not cut sharply at threshold (i.e.  $PM_{2.5}$ )
- number concentration can be made traceable (sort of)

# Measurement Issues (II)

## Reliability and Repeatability

- difficult to establish

## Uncertainty

- large uncertainties (can be order of magnitude in number, factor of 2 in mass)

## Reference Materials

- airborne particulate RMs don't exist

## Representativeness

- all ex-situ methods suffer from sampling issues
  - how representative is the sample at the measurement location of the airborne particulates?
    - losses, agglomeration, evaporation/condensation

# Measurement Issues (III)

## Measuring properties with different methods

- most instruments are proprietary
  - each manufacturer implements a different measurement principle
- difficult to intercompare results obtained with different instruments
- examples
  - size
    - mobility diameter, aerodynamic diameter, geometric diameter, radius of gyration
  - black carbon mass
    - directly measured, or inferred from optical absorption, extinction, or emission measurements

# Measurement Issues (IV)

## Measuring specific properties with a myriad of interferences

- selectivity
  - how does one measure properties of one component of PM when many others are present?
- sensitivity
  - atmospheric concentrations are often very low ( $<1 \mu\text{g}/\text{m}^3$ )
- gas composition
  - can be highly variable
  - can influence measurement
- morphology
  - spherical particles vs. fractal aggregates
- single particle vs. ensemble measurements
- variations over time, elevation, temperature, humidity, sunlight, etc.

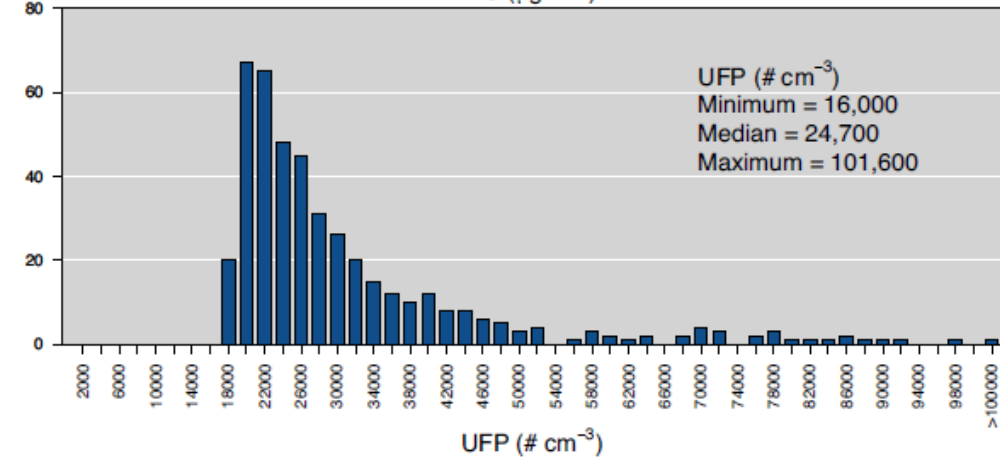
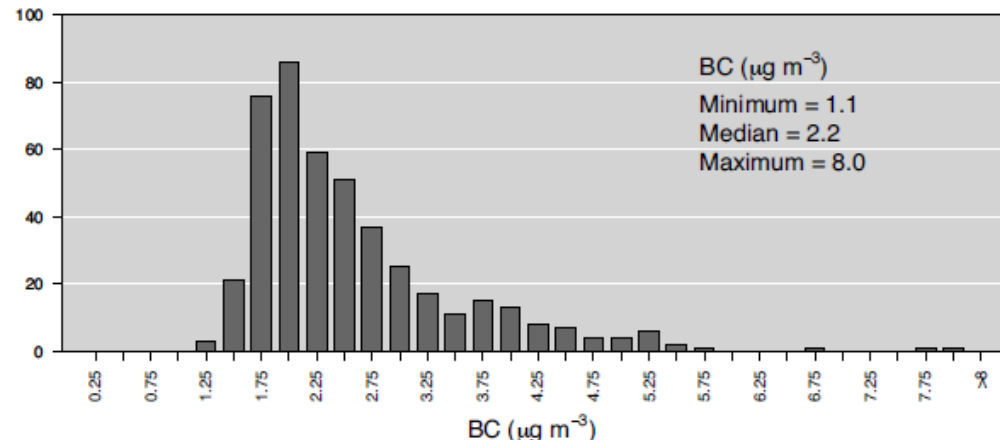
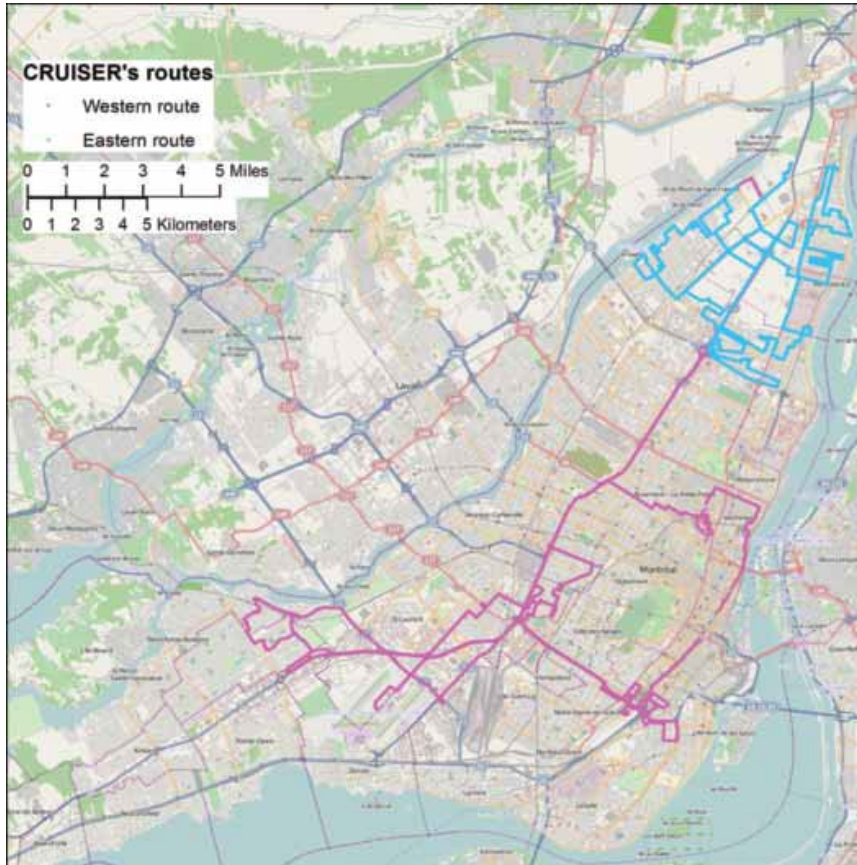


# What is the Canadian perspective on research and monitoring of airborne particulates?



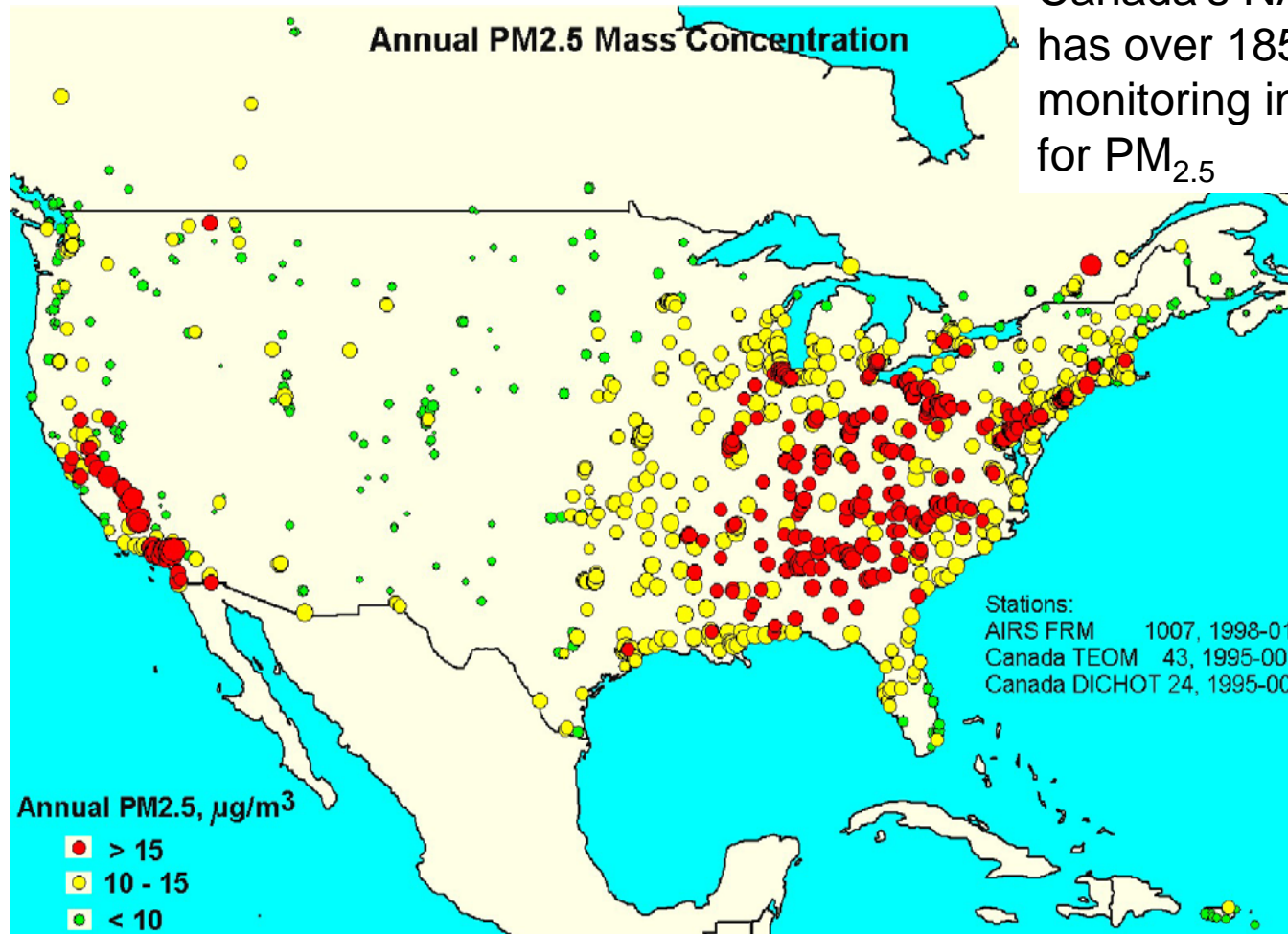
Jeff Brook, Environment Canada

# CRUISER Mobile Lab Survey in Montreal (2009)



Jeff Brook, Environment Canada

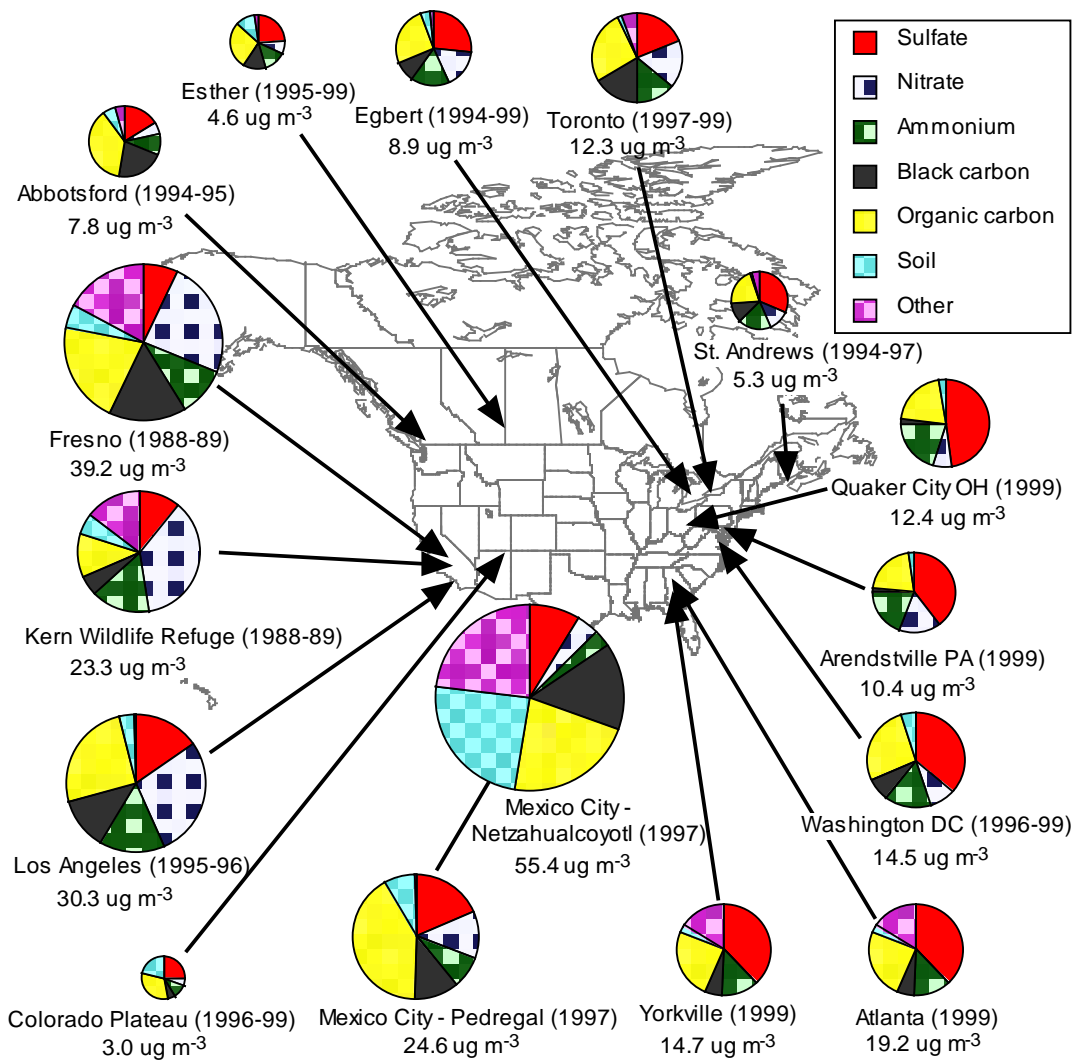
# North American PM<sub>2.5</sub> Measurements



Canada's NAPS network has over 185 real-time monitoring instruments for PM<sub>2.5</sub>

Jeff Brook, Environment Canada

# PM<sub>2.5</sub> Composition in North America

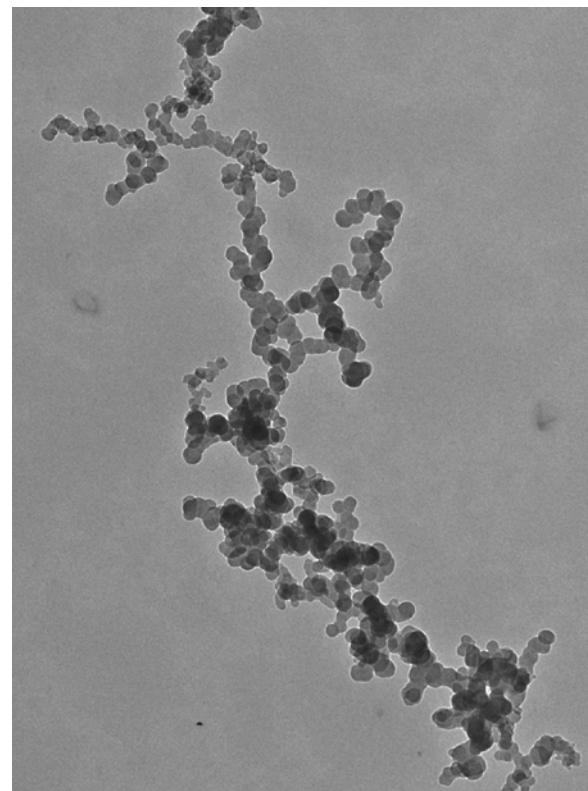


Jeff Brook, Environment Canada

# What is Canada doing about the measurement of black carbon?

*“Black Carbon is a distinct type of carbonaceous material that is formed primarily in flames, is directly emitted to the atmosphere, and has a unique combination of physical properties”*

- strongly absorbs visible light
- is refractory with a vaporization temperature near 4000 K
- exists as an aggregate of small spheres
- is insoluble in water and common organic solvents



Bond et al., “Bounding the role of black carbon in the climate system: A scientific assessment,” *Journal of Geophysical Research – Atmospheres*, 2013

# Confusion around BC definition

**refractory carbon**

**brown carbon**



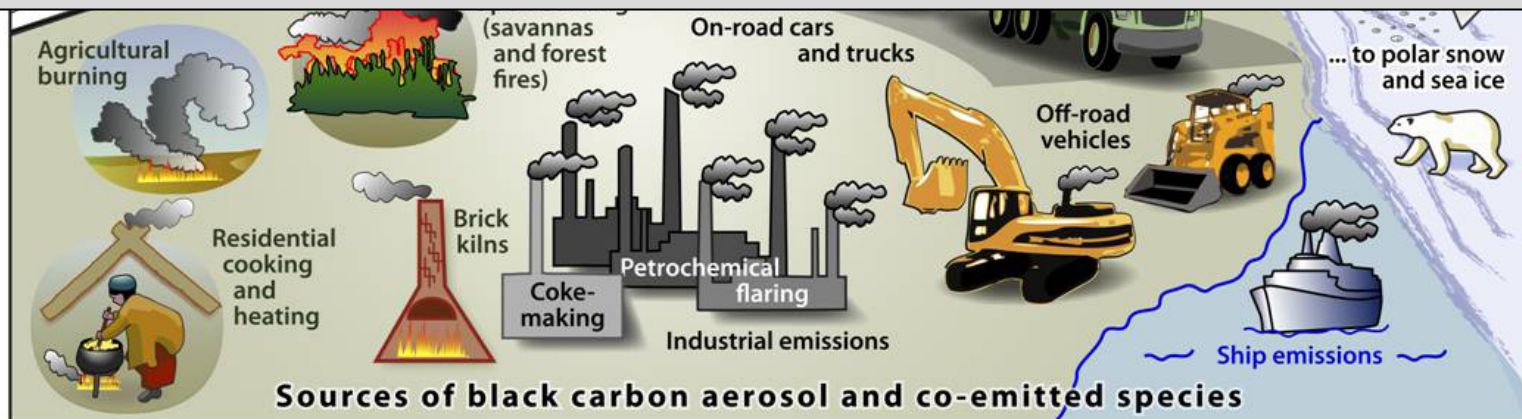
**elemental carbon**

**soot carbon**

**black carbon**

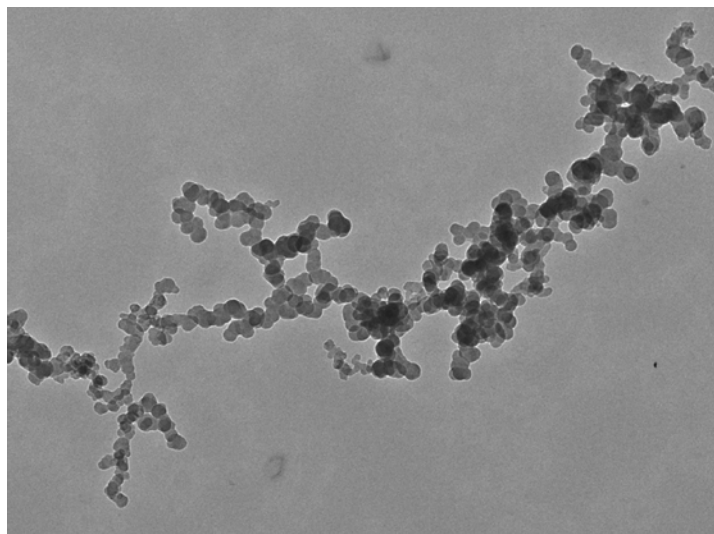
**light absorbing carbon**

- overall impact of BC estimated as  $+ 1.1 \text{ Wm}^{-2}$ 
  - $\text{CO}_2$  and  $\text{CH}_4$  are 1.56 and 0.86, respectively
  - this is higher than previously estimated
  - BC is the 2<sup>nd</sup> most significant climate forcer
- recognized by Climate and Clean Air Coalition (CCAC) as a significant short lived climate pollutant
- diesel engines produce 70% of BC emissions in NA
- engine technologies and fuels are changing and there is a need to understand the impact of these new changes on BC emissions and emission measurements

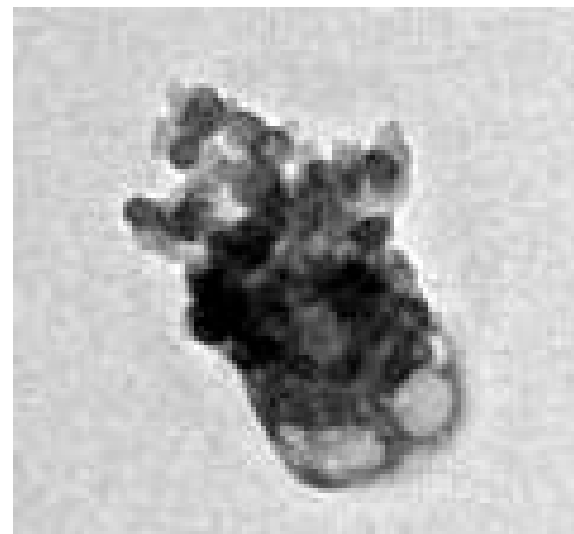


# Black Carbon Aging in the Atmosphere

- as BC surface oxidizes in the atmosphere, coatings will be deposited
  - lead to collapse, changing the morphology of the particles
- uncertainty around how these coatings and morphology changes influence the radiative properties of BC



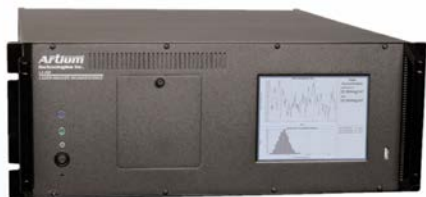
freshly emitted BC – fractal morphology



aged BC – compact structure



# Examples of BC and PM measurement instruments



Laser Induced  
Incandescence



Thermal Optical  
EC/OC Analyzer



Gravimetric



Centrifugal Particle  
Mass Analyzer



HR-TEM



Electrostatic  
Precipitator



Fast Particle  
Mobility Size  
Spectrometer



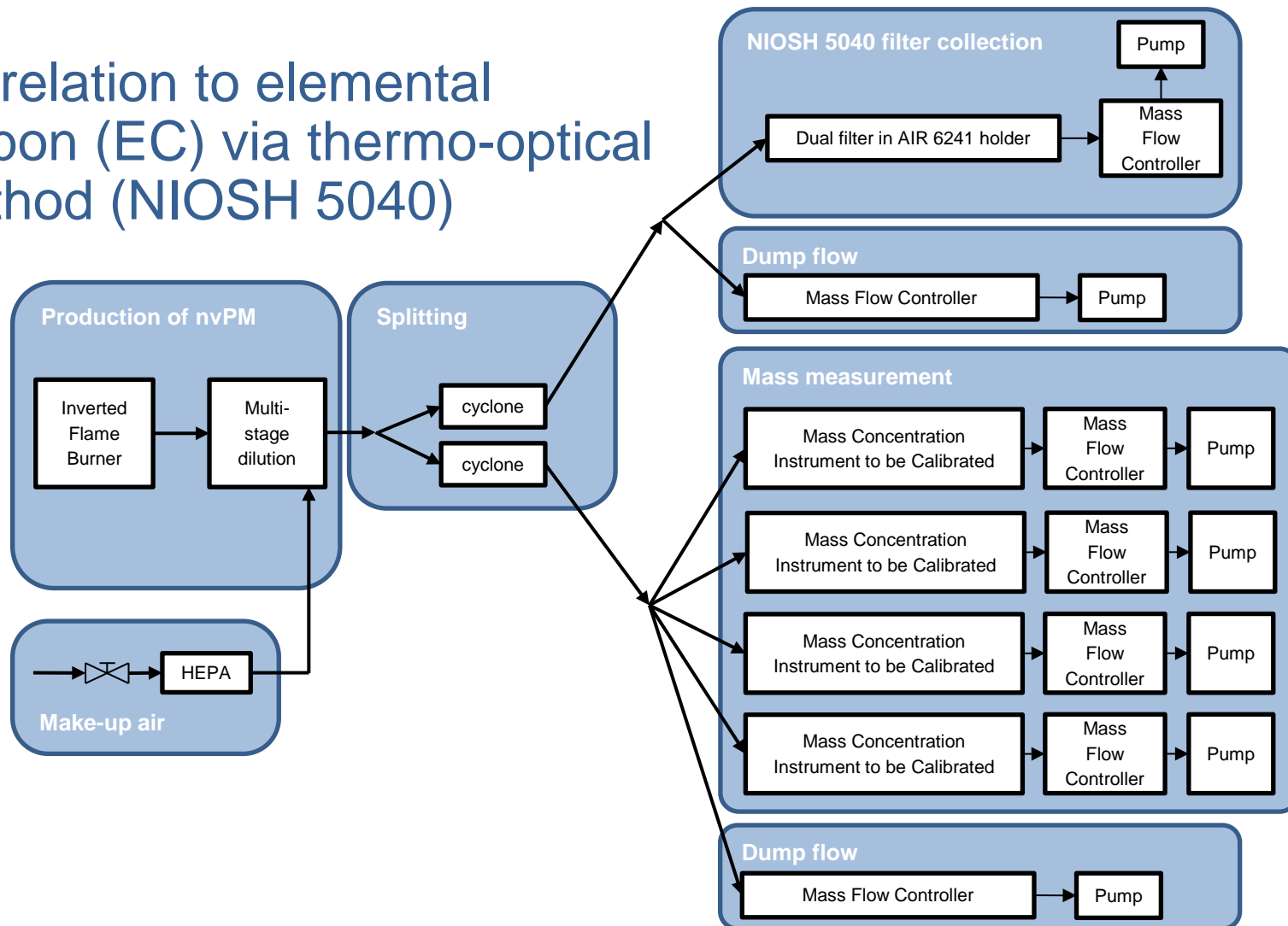
Scanning Mobility  
Particle Sizer



Condensation  
Particle Counter

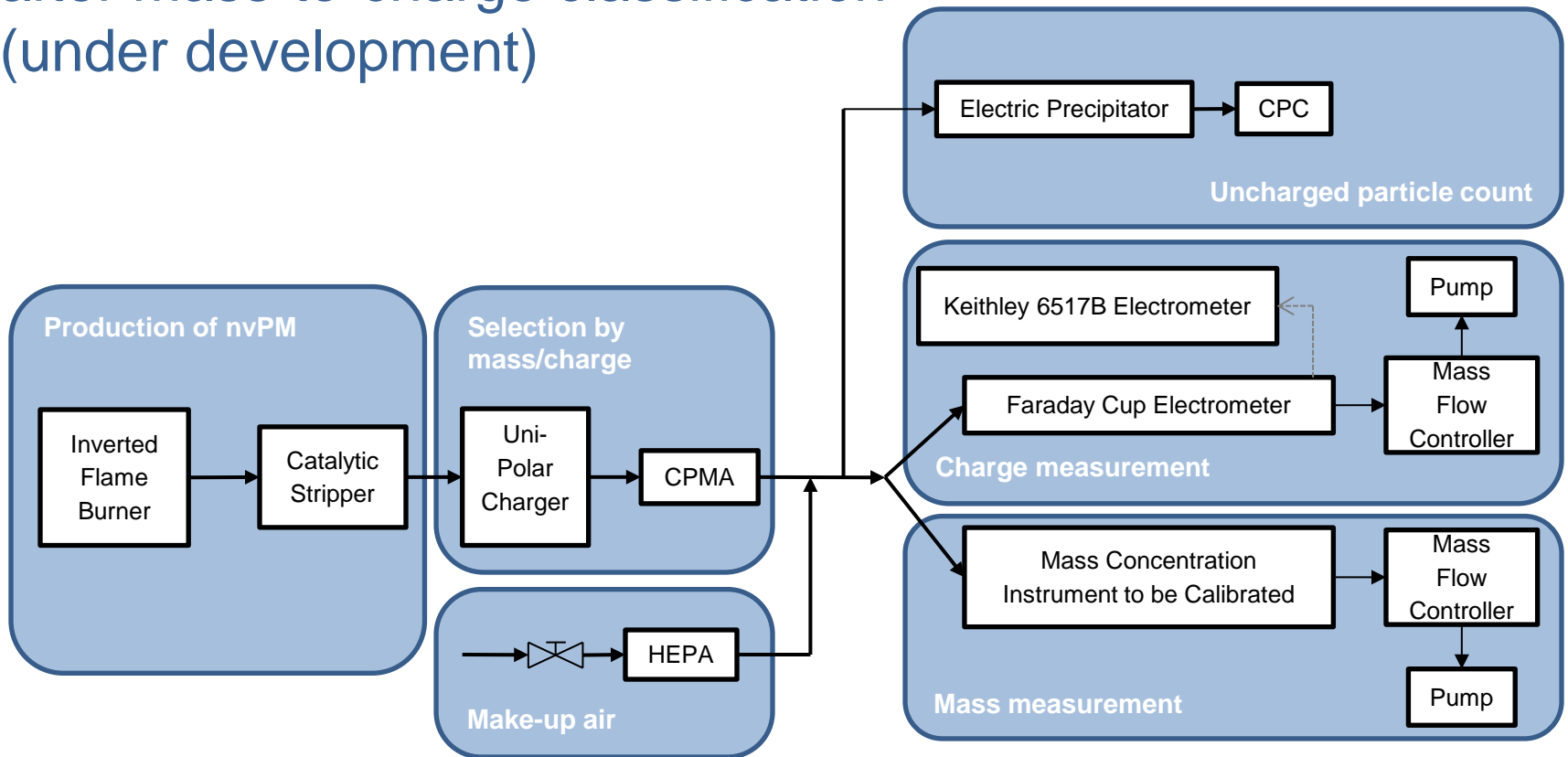
# Development of BC Mass Calibration (I)

Correlation to elemental carbon (EC) via thermo-optical method (NIOSH 5040)



# Development of BC Mass Calibration (II)

Correlation to electrical charge after mass-to-charge classification (under development)



## Summary (I)

Airborne particulate matter has significant, detrimental effects on health, visibility, and climate

- $PM_{2.5}$  mass concentration measurements, while important, are a poor overall indicator of these effects

PM metrology is required

- to improve reliability and repeatability of measurements, and to reduce uncertainty
  - critically important to climate change modelling
  - necessary to improve association between health effects and PM properties
- for sound policy decisions and regulations

## Summary (II)

Quality of measurements and intercomparability need to be improved

- size and size distribution
- composition
- surface area and surface reactivity
- optical properties (absorption and scattering)
- mass of smaller size fractions ( $PM_{1.0}$ )

Black Carbon is one of the best PM targets due to co-benefits in reducing climate forcing and improving human health



# Thank you

Dr. Gregory J. Smallwood

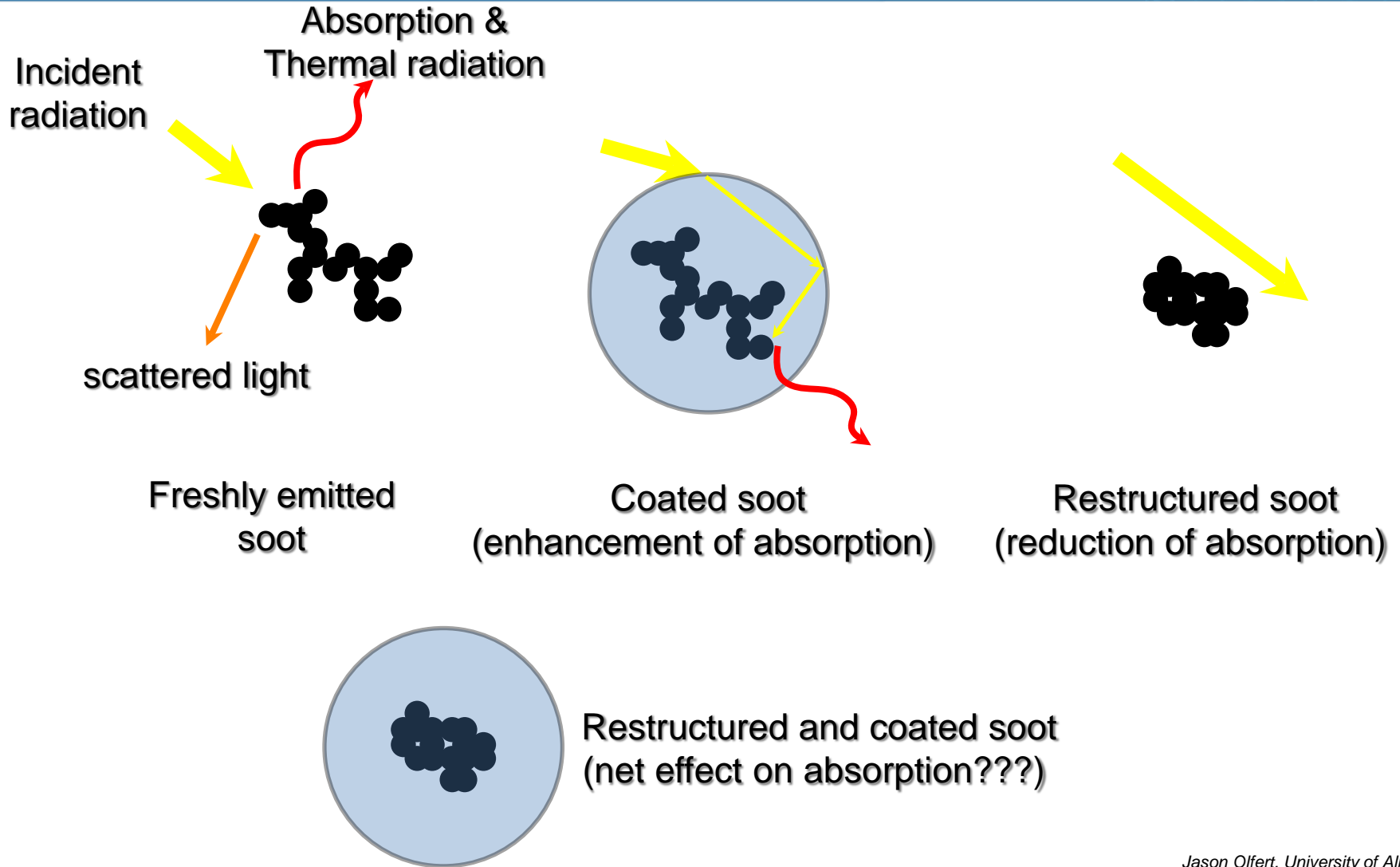
Program Leader, Measurement Science for Emerging Technologies

phone: 613-993-1391

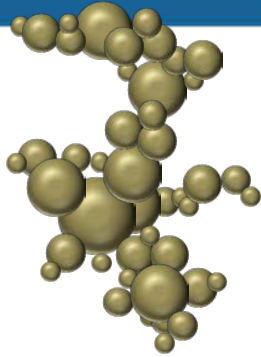
e-mail: [greg.smallwood@nrc-cnrc.gc.ca](mailto:greg.smallwood@nrc-cnrc.gc.ca)

web: [www.nrc-cnrc.gc.ca](http://www.nrc-cnrc.gc.ca)

# Variations in Optical Absorption



## Black carbon metrics of importance



Black carbon often consists of highly non-spherical agglomerates of non-uniform primary particles

Radiative forcing	$\propto$ Mass concentration of BC
Cloud condensation	$\propto$ Number concentration of BC
Chemical reactions	$\propto$ Surface area concentration of BC
Health impacts	$\propto$ Mass, number and surface area concentration of BC
Particle settling	$\propto$ Mass of individual particle
Advective transport	$\propto$ Non-spherical drag coefficient, dynamic shape factor



# BC Characterization – not just mass and number

## common indicators of interest

- mass concentration (environment)
- number concentration (health)

## additional parameters important to understand the true impacts of BC

- spectral light absorption characteristics
- detailed morphology
- active surface area (chemical/thermal)
- primary particle diameter distribution
- aggregate size distribution
- optical properties
- volatile fraction
- chemical composition

improved characterization of all parameters is important to reducing the uncertainty associated with black carbon's role in climate forcing

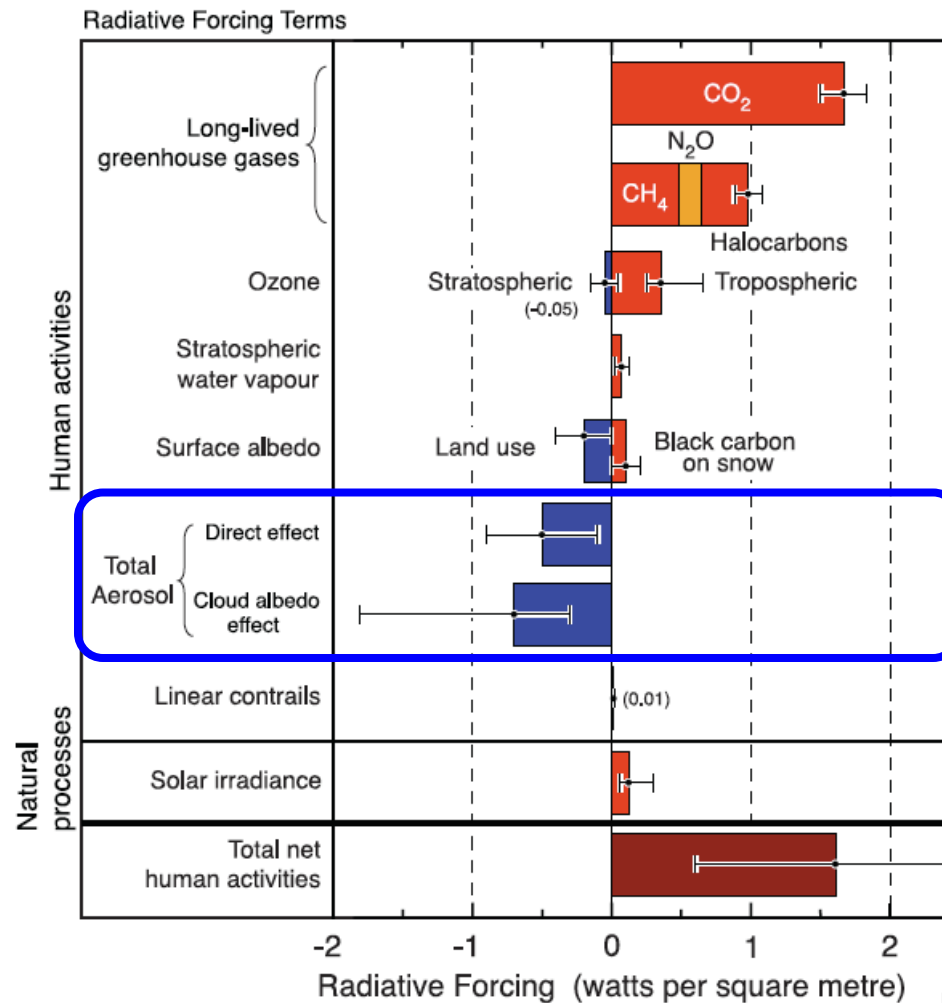
# Activities Known to Emit Carbon Particles

Sources of Carbon Particles	Biogenic	Anthro-pogenic	Black Carbon	Organic Carbon
Wood Combustion (stoves, wild fires)	●	●	●	●
Gasoline vehicles		●	●	●
Heavy duty diesel (on-road, off-road, ships)		●	●	●
Tire wear, brakes, road dust		●	●	●
Leaf litter and leaf waxes, spores, bacteria	●			●
Aircraft		●	●	●
Natural gas combustion		●	●	●
Tobacco smoke		●	●	●
Steel production and coke ovens		●	●	●
Fuel oil boilers		●	●	●
Cooking of meat, vegetables, use of cooking oil		●	●	●
Coal combustion		●	●	●
Road paving		●		●
Roofing tar pots		●	●	●

Jeff Brook, Environment Canada

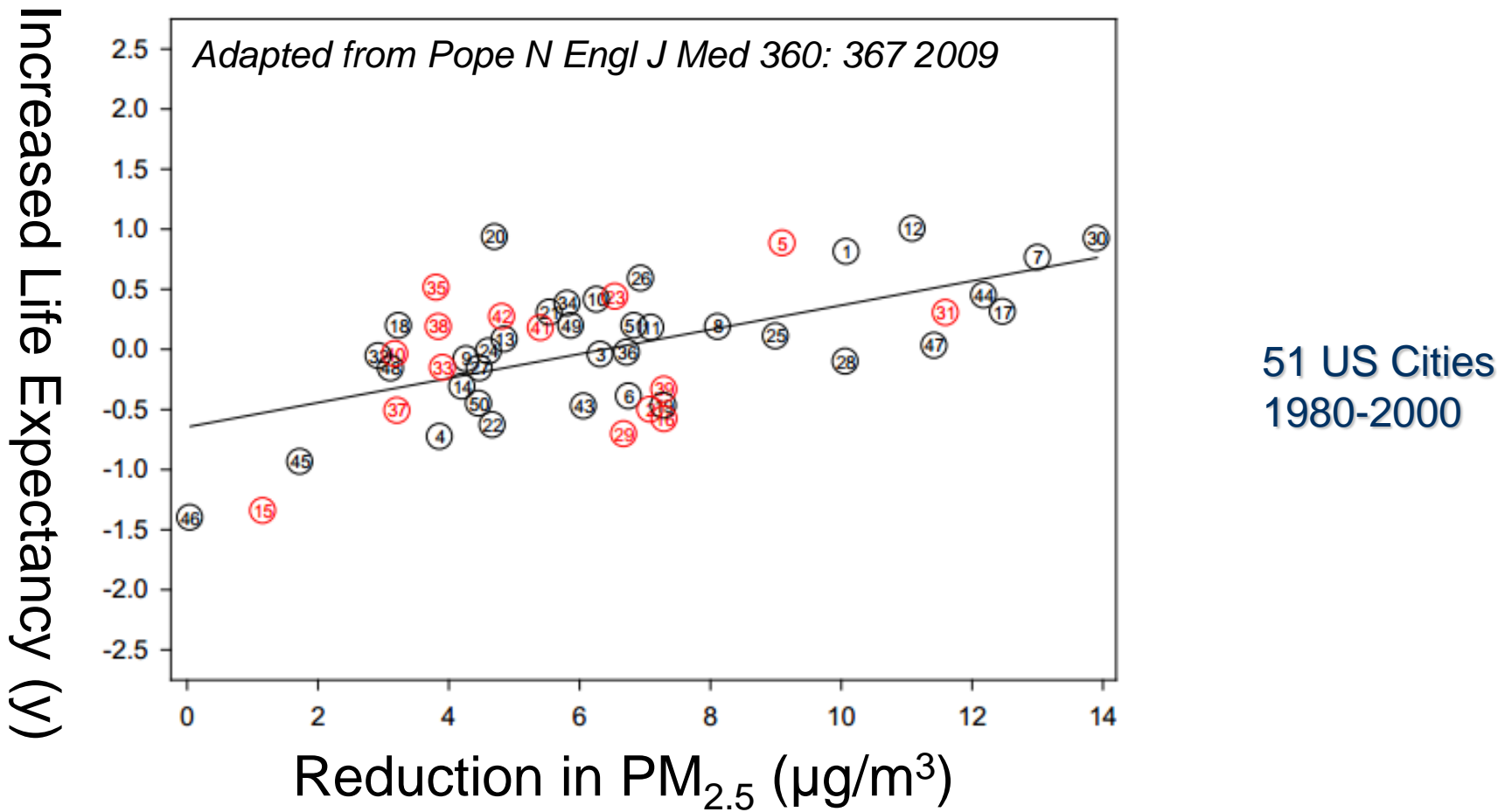
# Relative Effect of Aerosols on Climate

Radiative forcing of climate between 1750 and 2005



Intergovernmental Panel on Climate Change (2007)

# Trend 1: Is improving air quality benefiting health?

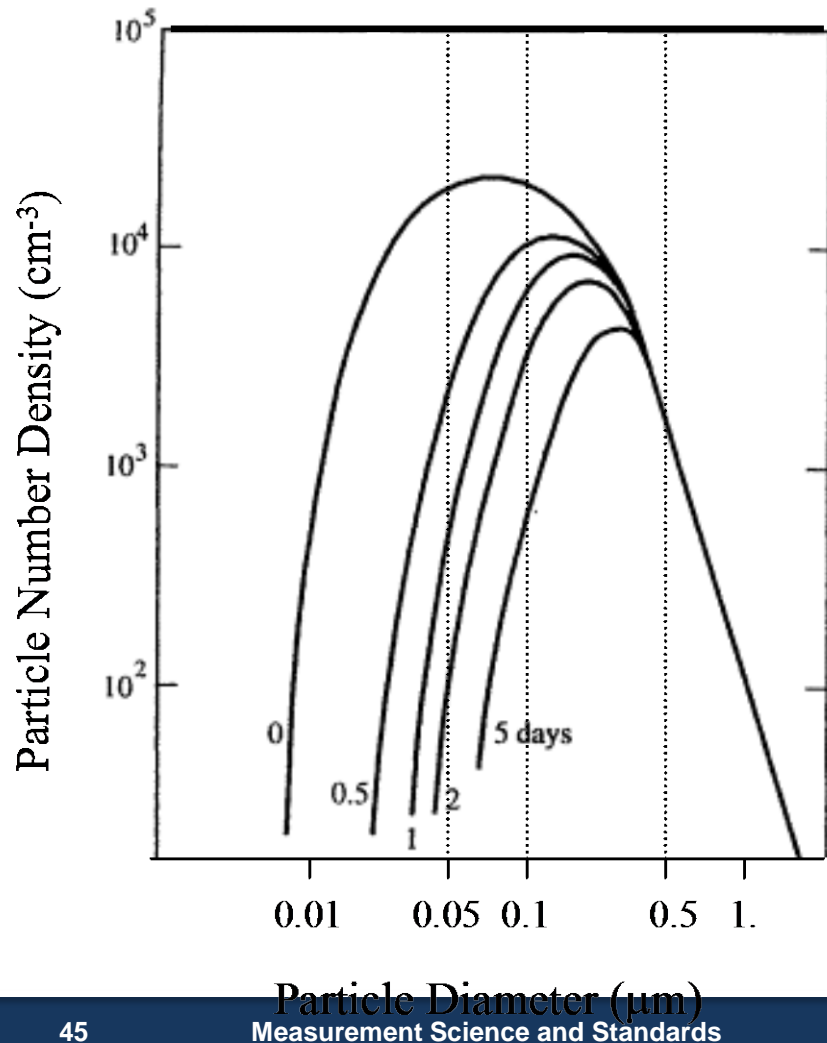


Reduced pollution yields increased life expectancy

Greg Evans, University of Toronto

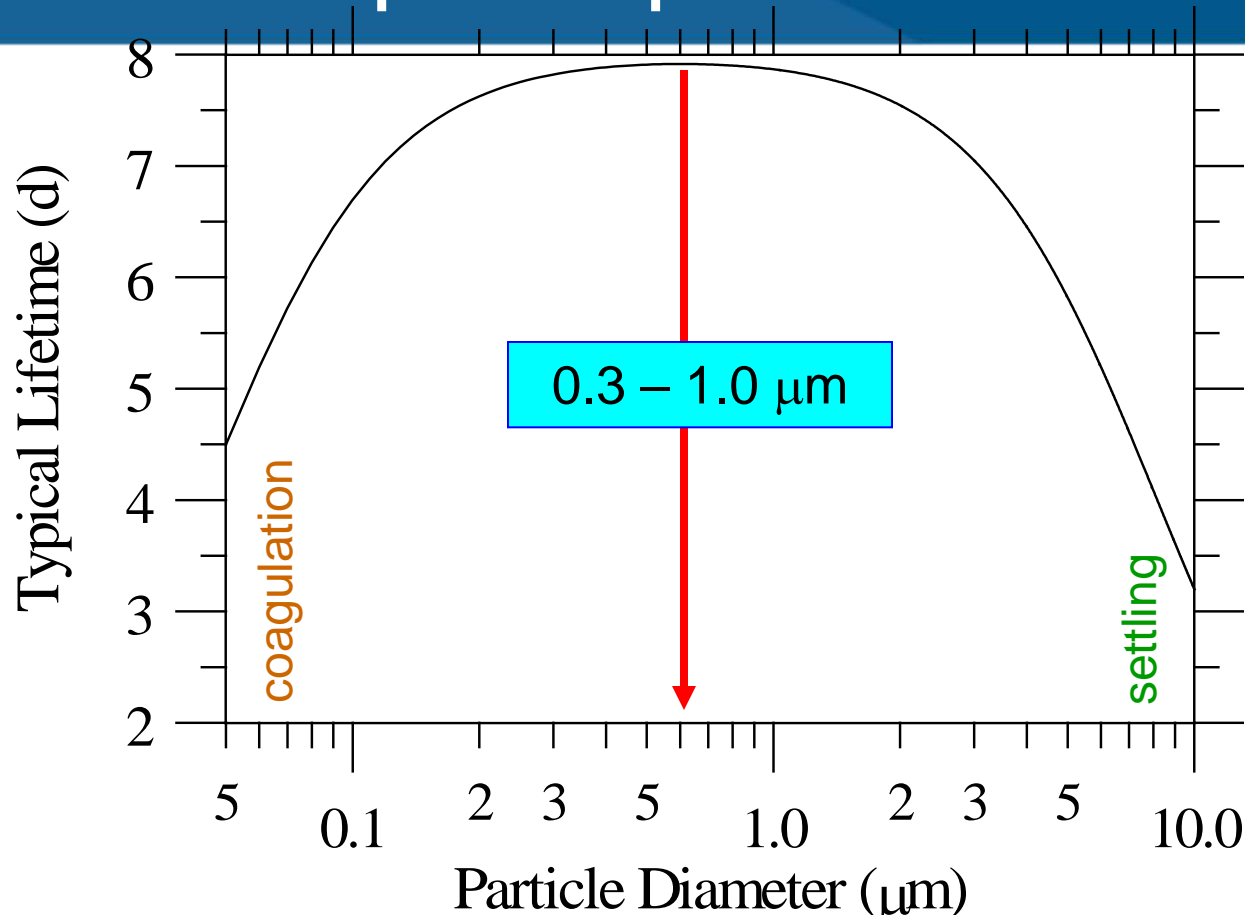
# Lifetime of Ultrafine Particles

Change in distribution due to coagulation



- The number of nuclei mode particles (<10 nm) last less than half a day
- Ultrafine particle number reduces by at least an order of magnitude in a day and a half
- Beyond 2 days the bulk of the particles have grown into the accumulation model
- Result: total number reduces and mass concentrates in accumulation model

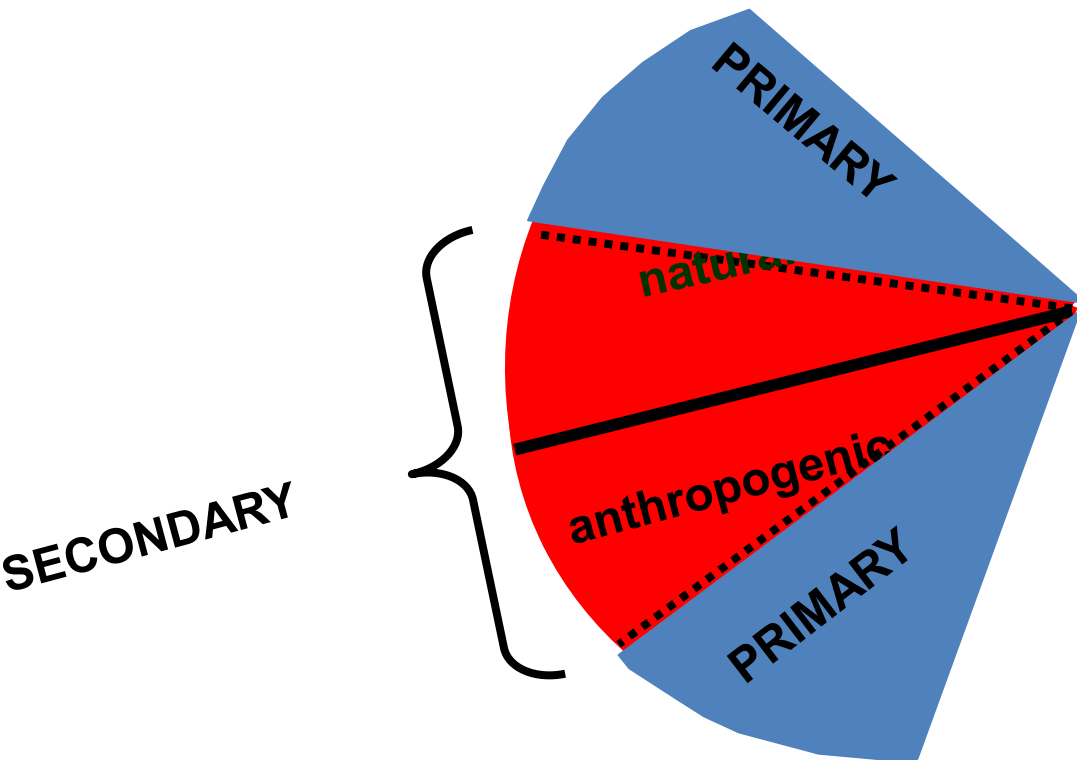
# Lifetime in Atmosphere Depends on Size



- Wet and dry deposition are the main loss mechanisms
- Deposition velocity is slow (0.1-1.0 cm s<sup>-1</sup>) and interception of rain drops is relatively inefficient

Jeff Brook, Environment Canada

# General Apportionment of Organic Carbon (OC)



## BIOGENIC

(primary and secondary)

- cannot be controlled, but must be quantified relative to anthropogenic fraction

## ANTHROPOGENIC

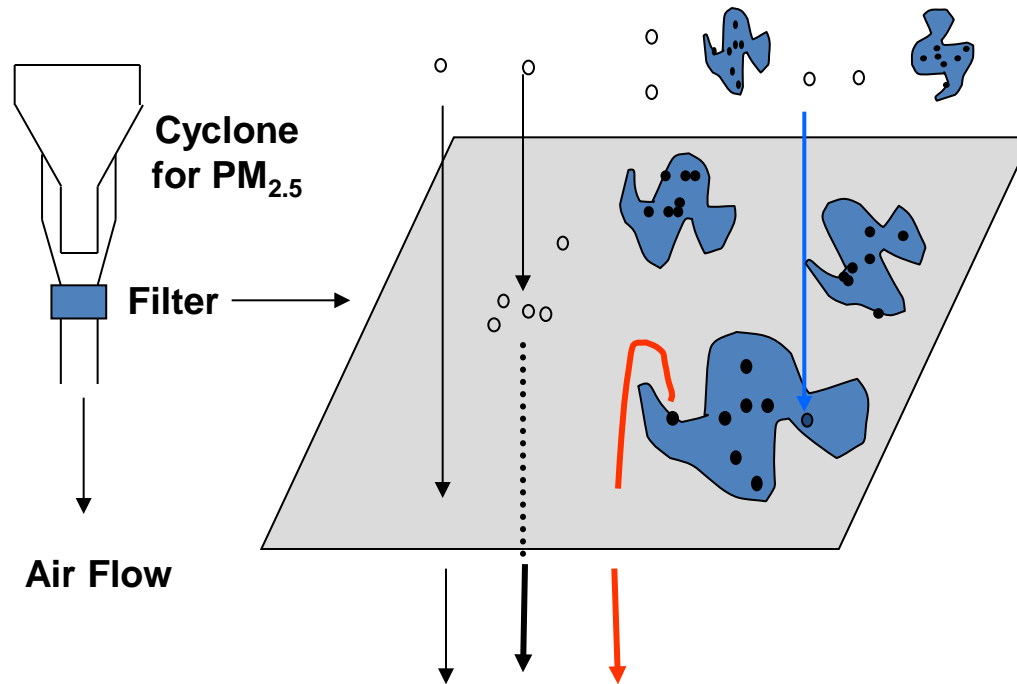
- can be controlled
  - need to know relative amounts of primary and secondary OC
  - need to know main sources of both fractions
- “specific apportionment”

OC is the least understood fraction

# Sampling Artifacts due to Semi-Volatiles

## Molecule Interactions during Air Sampling

- --- in gas
- --- in PM

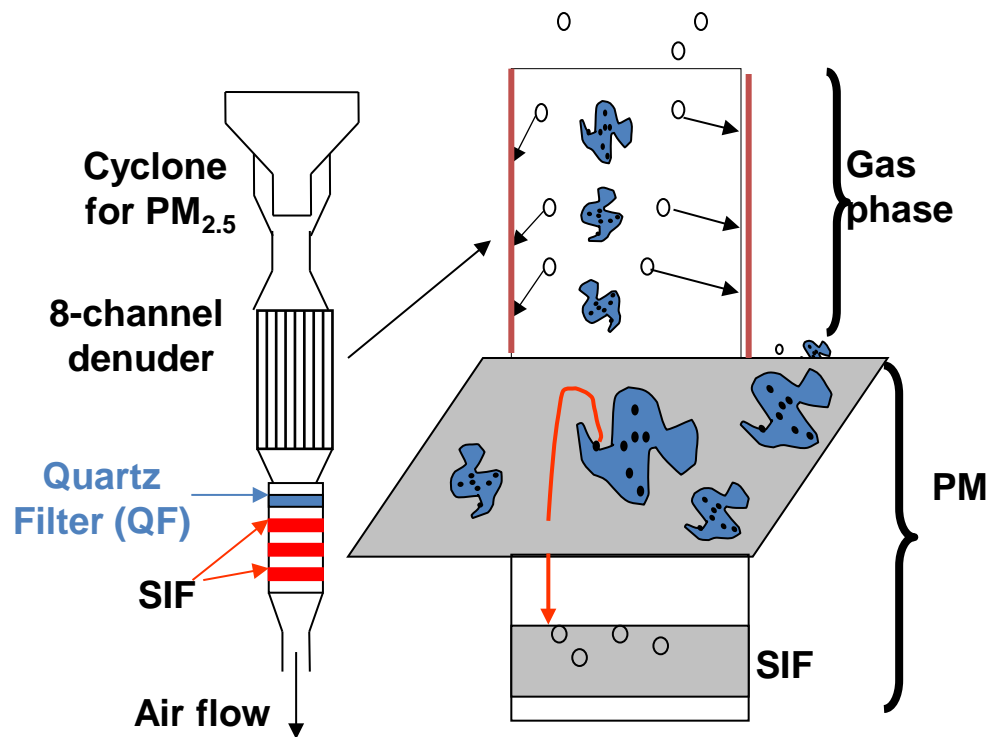


## Traditional Filter Pack (FP) Sampler

Jeff Brook, Environment Canada



# Sampling approach for reducing artifacts



## Integrated Organic Gas and Particle Sampler (IOGAPS)

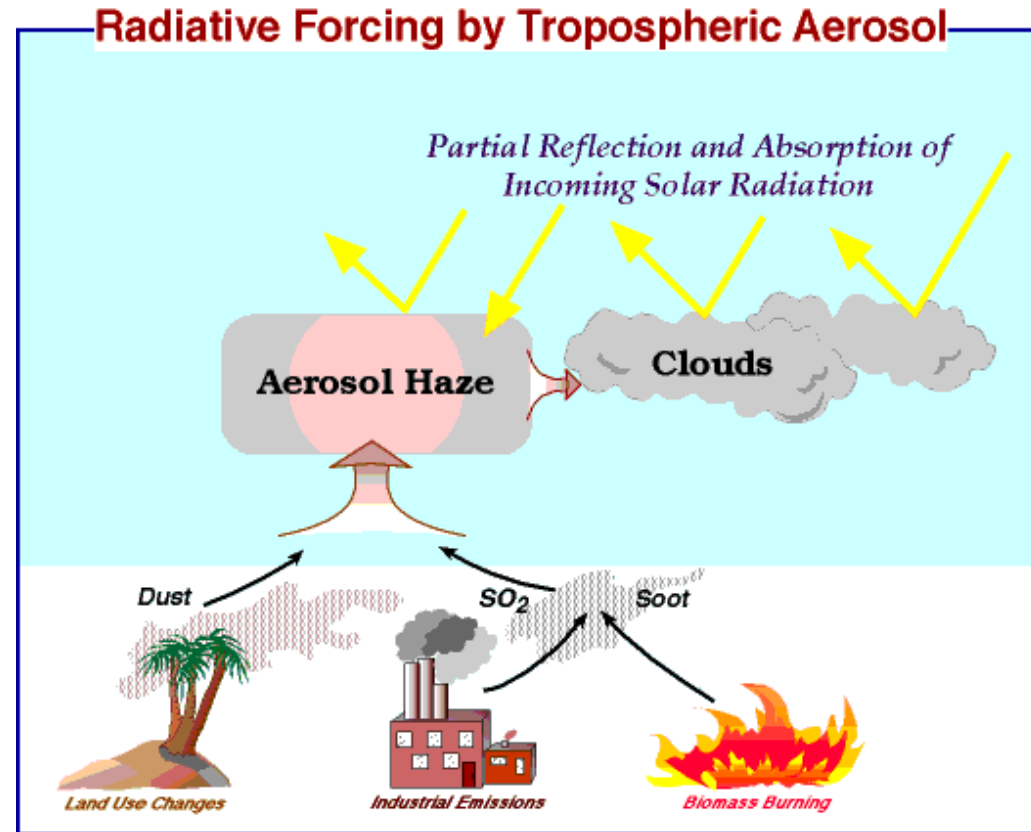
# Why They are Important (Continued) Modify the Earth's Climate

## Indirectly Modify Climate

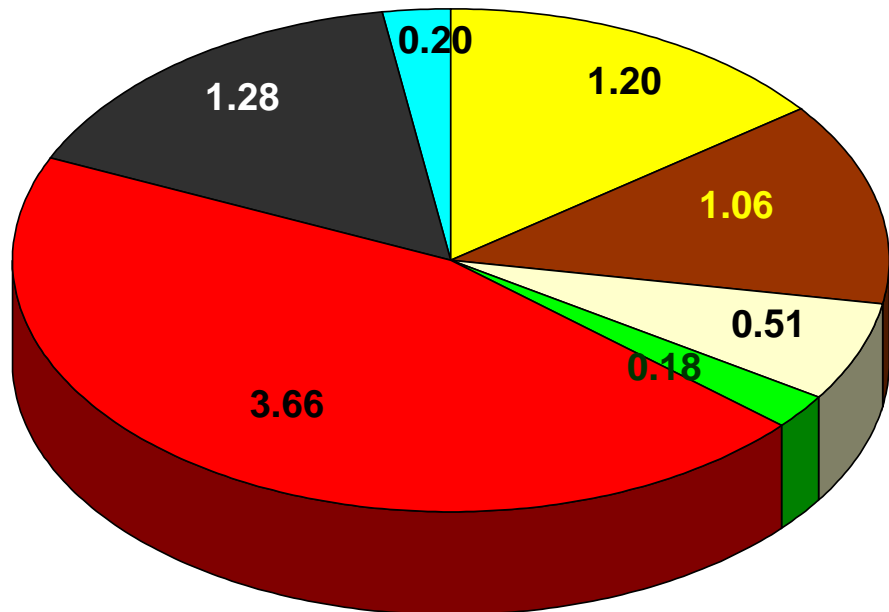
- by acting nucleation sites for clouds
- If act as nucleation sites they can change the frequency of clouds and the size of cloud droplets → change the amount of light the clouds scatter

**Key point:** Aerosols can have a large effect on the Earth's radiation budget → The radiative forcing by Anthropogenic aerosols is believed to be the same order of magnitude as the radiative forcing by CO<sub>2</sub>

**Key point:** To understand and predict climate change and make effective policy decisions on climate change need to understand atmospheric aerosols and their role in climate!!

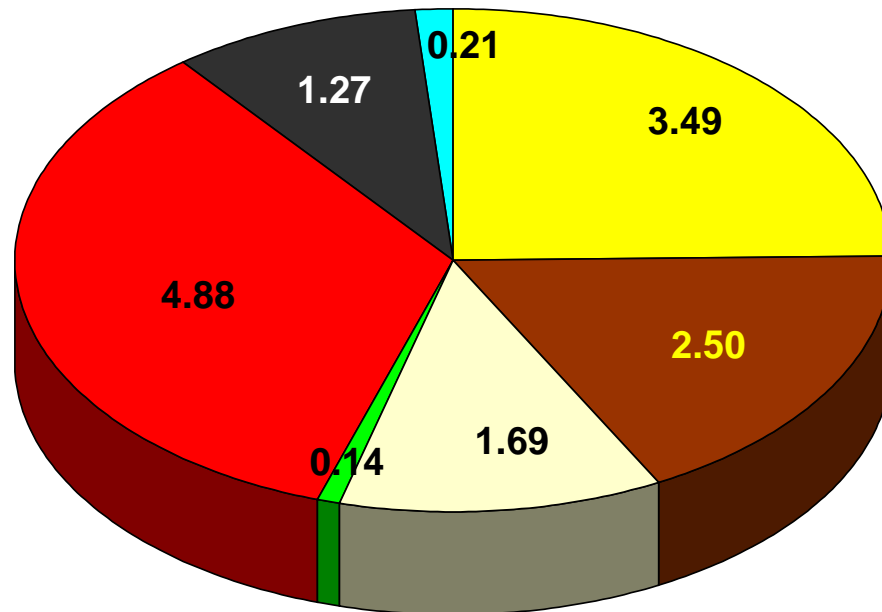


# Comparison of Two Canadian Cities



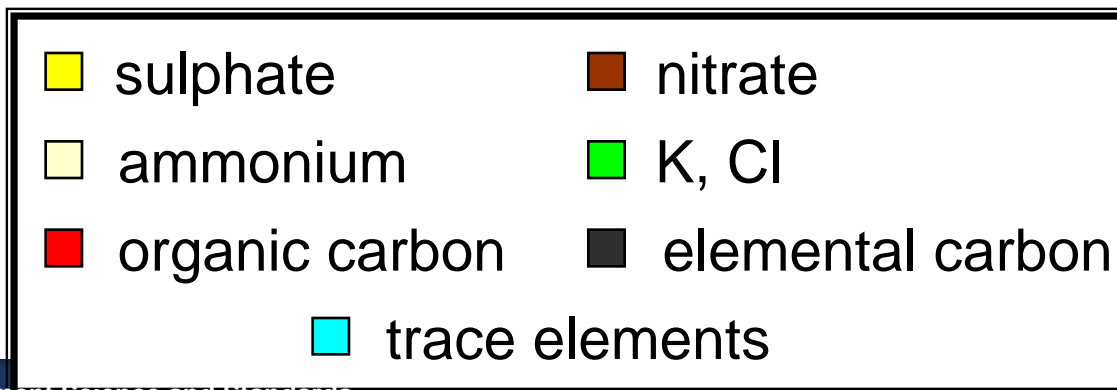
Vancouver 9.5 µg/m<sup>3</sup>

61% C



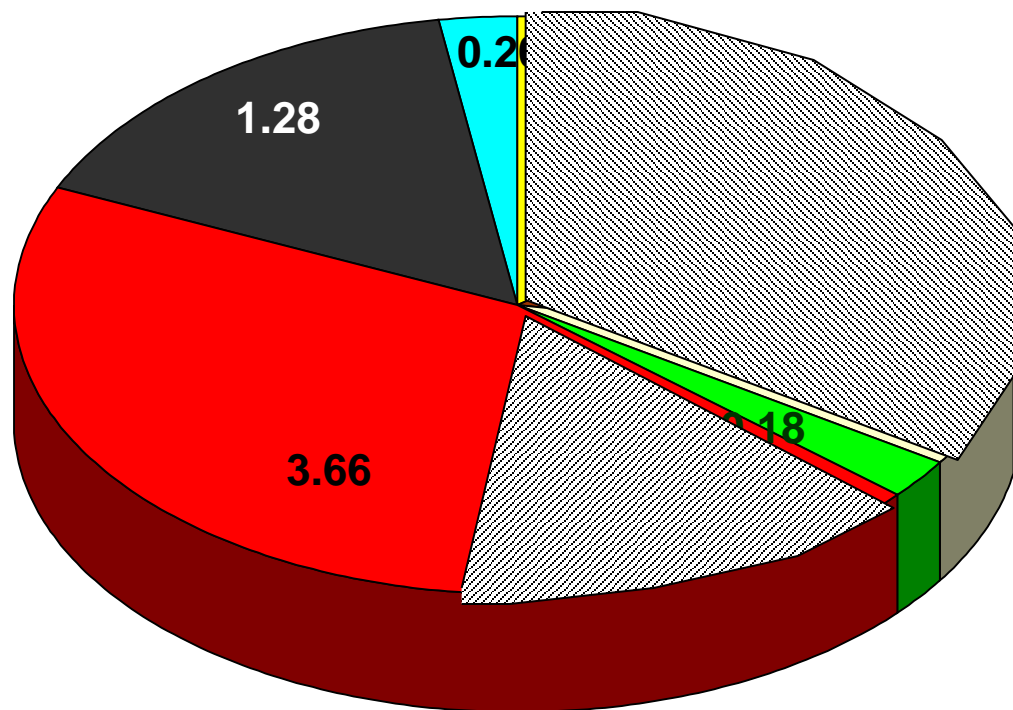
Toronto 14.2 µg/m<sup>3</sup>

43% C



Jeff Brook, Environment Canada

# Amount of PM<sub>2.5</sub> from Secondary Formation



Vancouver 9.5 µg/m<sup>3</sup>

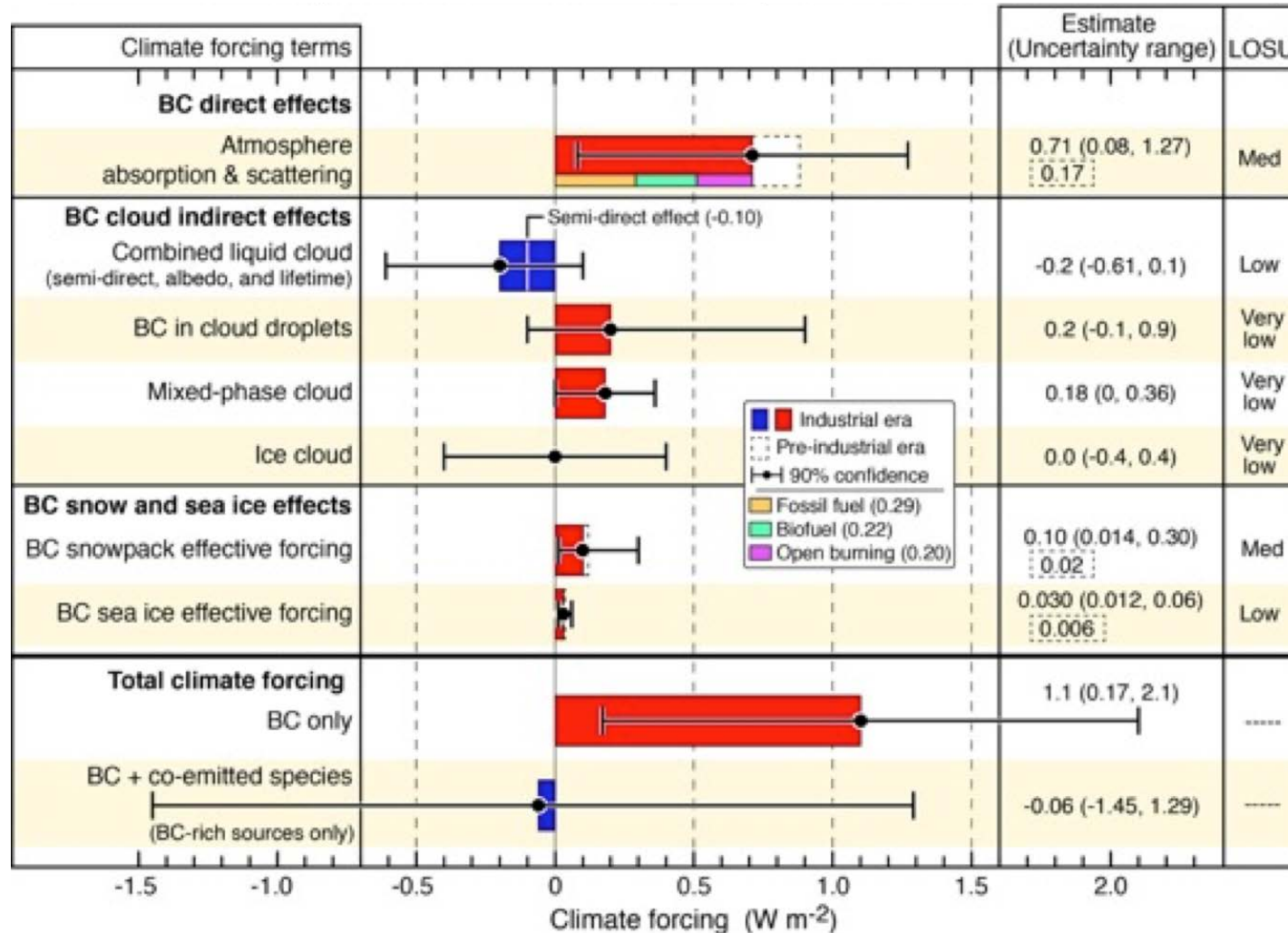
Sulphate	1.2
Nitrate	1.1
Ammonium	0.5
20% of OC	0.75

**3.5**

**37% of PM<sub>2.5</sub>  
is secondary**

Jeff Brook, Environment Canada

# Global Climate Forcing of Black Carbon



T. C. Bond et al., *Bounding the role of black carbon in the climate system: A scientific assessment*, *Journal of Geophysical Research-Atmospheres*, doi: 10.1002/jgrd.50171, 2013.